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THE STUDY OF THE
SYNTHESIS OF GLYCEROL

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STUDY OF SYNTHESIS OF GLYCEROL

by

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I. INTRODUCTION

The synthesis of glycerol presents one promising solution to a pressing problem in regenerative life support systems, i.e., the continuous production of human energy sources from metabolic waste materials. Of various proposed compounds, glycerol appears to be among the easiest to synthesize and purify. In addition, preliminary nutritional evaluation has been favorable. Glycerol has been proposed by various workers as a promising source of metabolic energy (calories) on board a spacecraft (1,2,3). The nutritional value of glycerol has been established (3,4,5). It has been fed at levels up to 41% with no deleterious effects and has been shown to act as a source of dietary energy (4). Glycerol is easier to synthesize than more complicated compounds, such as fatty acids and lipids, and appears to be among the most promising candidates as a calorie source in a closed-loop life support system.

There are a variety of potential chemical routes to glycerol starting with simple metabolic wastes such as CO_2, and water or their immediate derivatives, H_2, O_2, CH_4 and HCHO. These include:

1. Synthesis based on Propylene
2. Synthesis from Acetylene and Ethylene
3. Direct Hydrogenation of Carbon Monoxide
4. Hydrogenation of Carbohydrates
5. Trimerization of Formaldehyde

Frankenfeld of Esso Research and Engineering Company (1) completed a comprehensive study of all these potential methods and concluded that the most promising method for the synthesis of glycerol from metabolic wastes are those based on formaldehyde. In response to RFP A13053 (HK-34) Esso Research and Engineering Company prepared a proposal (6), of which Phase I was ultimately accepted as The Study of the Synthesis of Glycerol, Contract NAS2-4496.

This study consisted of a laboratory effort directed toward identification of a reaction sequence suitable for the production of glycerol in a spacecraft environment. Process should be a continuous one capable of producing 5 Kg/day of CP pure glycerol for 500 days. Starting materials can include CO_2, CO, O_2, CH_4, H_2, H_2O and CH_2O.

Consideration of the known chemistry in light of technical possibility, toxicity of by-products and of space economics indicated that the most promising route to glycerol involved use of formaldehyde as the starting material. Two routes were thus considered as part of the study:

1) Trimerization of formaldehyde to glyceraldehyde and dihydroxyacetone followed by hydrogenation to glycerol.

2) Condensation of formaldehyde to 6-carbon sugars followed by reductive cleavage to glycerol.

The major goal of The Study of The Syntheses of Glycerol was to select the most promising route for the continuous production of 5 Kg/day of "pure" (CP) glycerol. Thus the major emphasis was on the chemistry of the system, including a definition of a number of parameters of the system including kinetics, heterogeneous and homogeneous catalysis and other basic variables of the system.

II. HOMOGENEOUS FORMALDEHYDE CONDENSATION REACTION STUDIES

A number of studies on the self-condensation of formaldehyde in water have been made. Homogeneous reactions were carried out to (1) substantiate prior work (2) develop a fundamental understanding of the formaldehyde reaction system in a simple homogeneous system and (3) provide a source of formose sugars for the development of analytical procedures. It was anticipated that these data could be applied to the more complex heterogeneous reaction system. Heterogeneous reaction studies employing exploratory alkaline earth metal oxide type catalysts were also carried out.

A. Preliminary Homogeneous Exploratory Runs

A number of preliminary exploratory runs were made in a simple batch reactor system. In these runs, a half mole of formaldehyde in 200 ml of aqueous solution (+ incidental methanol from the formaldehyde solution) was added to a small flask. A run was made by adding the chosen catalyst or catalyst combination, inerting the flask with a nitrogen atmosphere, heating and stirring the mixture by means of a magnetic stirrer. The results of each run are summarized in Table 1. The reaction is quite fast with $Ca(OH)_2$ at 75°-80°C, and one can determine if any reaction is occurring at these conditions by a rapid color build-up and complete removal of CH_2O (by odor). These runs showed that at 25 to 60°F $CaCO_3$ and $Ba(OH)_2$ did not catalyze the condensation of the CH_2O. On the other hand, even at room temperature $Ca(OH)_2$ produced a high yield of almost colorless product. Studies carried out in the presence of oxygen indicate that the use of a nitrogen atmosphere seems to retard the build-up of color bodies.

These products provided a source of formose sugars for the development of our analytical procedures. A G.C. technique similar to that described by Sweeley (7) was developed. The formose sugars are derivatized to the trimethylsilylated products and then analyzed by G.C. The procedure and interpretation are described in the Experimental Section of this report. The data show these products to be extremely complex containing 40-50 components including both low molecular and high molecular weight sugars. The G.C. curves may be found in the Appendices. The presence of hemi-formals is indicated by the smearing of peaks, indicating they have a retention time greater than the parent sugars but considerably less than the next higher sugars.

B. Fundamental Investigations of Formaldehyde Condensation in a Homogeneous Reaction System

As part of our effort to develop a fundamental understanding of the formaldehyde condensation reaction, we studied the effect of reaction variables and the role of various co-catalysts in the system. These studies used the batch reactor system, as previously discussed. This system has the advantage of being relatively simple, rapid, and it allows the study of a wide range of variables. In all runs oxygen was excluded by use of a nitrogen sparge and the reaction was terminated by our carbon dioxide quenching technique. All of the results which we will discuss below are summarized in Table II.

1. Effect of Temperature and Time on
   Formaldehyde Conversion and Selectivity

The effect of temperature on HCHO conversion and selectivity was
studied at a standard $HCHO/Ca(OH)_2/Glucose$ ratio. (0.18m/0.009/m/0.0018m).
At 40°C (runs 70-4 and 88-B) the conversion ranged from 4.8 - 8.3% with 100%
selectivity to C_2 and C_3 sugars. At 60°C (76-1) the conversion increased to
50%, however, the selectivity to a C_2 - C_3 fraction was greatly decreased.

We studied the effect of time on conversion using the same concen-
trations. The conversion ranged from 4.8 to 15.7% for 1 to 60 minutes, with
high selectivity in C_2 - C_3 material. Since the conversion was not sensitive
to time at 40°C, we undertook a similar series of runs increasing the tempera-
ture to 60°C. The conversion at 1 and 5 minutes was low (7-8%) and selectivity
to C_2 - C_3 material was high. The conversion increased to 50% at 10 minutes
and 82.6% at 30 minutes, but selectivity was greatly sacrificed.

Time, Min.

Temp. °C.	1	5	10	30	60
40	9.1% (88-C)		4.8% (70-4) 8.3% (88-B)		15.7% (76-10)
60	7.4% (76-3)	7.8% (76-6)	50.0% (76-1)	82.6% (76-4)	

HCHO 0.18m $Ca(OH)_2$/Glucose = 5/1
$Ca(OH)_2$ 0.009m   88-B and 88-C large scale, same ratio
Glucose 0.0018m   (run number)

These results show that the homogeneous formaldehyde condensation
reaction exhibits an induction period, and that the length of this induction
period is temperature dependent, i.e., higher temperatures reduce the length
of the induction period. Following the induction period an autocatalytic
reaction period appears to occur (i.e., a sharp increase in the rate of con-
version of CH_2O per unit time). The selectivity to lower sugars exhibits
a tendency to decrease as the conversion level is increased, which is as
would be expected in a step-wise condensation reaction system. This work
clearly indicates that temperature and reaction time must be carefully con-
trolled in the formaldehyde condensation system.

2. Effect of Formaldehyde Concentration

In order to determine the dependency of the system on HCHO concentration, a series of experiments was performed using 9, 18 and 37% HCHO at 60°C for 10 minutes with a fixed level of glucose (0.0018m) and Ca(OH)$_2$ (0.009m). The % conversion of CH_2O to sugars decreased with increasing concentration. At low conversion levels, however, the average rate of conversion of CH_2O was constant.

HCHO Conc.

	9% (0.18 m)	18% (0.36 m)	37% (0.72 m)
Conversion	50% (76-1)	8.0% (76-2)	3.8% (76-5)
Average rate moles CH_2O conv. per minute x 10^3	9.0	2.9	2 .7

60°C, 10 minutes
Glucose 0.0018 m
Ca(OH)$_2$ 0.009 m

(run number)

These results, although limited in quantity, suggest that the length of induction period is formaldehyde concentration dependent, with higher formaldehyde concentrations increasing the length of the induction period. The data indicate that during the induction period the actual rate of formaldehyde conversion does not change with concentration, i.e., a zero order dependence. These effects of concentration in the induction period could result from a kinetically complex reaction sequence or it could reflect the presence of extraneous compounds such as stabilizers in the formaldehyde solutions.

3. Effect of Varying the Catalyst and Co-Catalyst Ratios

We have studied the effect on CH_2O conversion of varying the catalyst and co-catalyst ratios. In addition to helping elucidate the CH_2O reaction system, from a practical standpoint, it is very desirable to be able to use lower concentrations of catalyst and co-catalyst.

Ca(OH)$_2$ Level

Glucose Level	0.0045 m	0.0090 m
0.0018 m	6.5% (76-13) [2.5/1]	4.8% (70-4) [5/1]
0.0009 m	4.6% (76-11) [5/1]	4.2% (76-12) [10/1]
.00018 m	1.4% (76-9) [25/1]	3.3% (76-8) [50/1]

10 minutes
40°C
HCHO - 9% solution

[Ca(OH)$_2$/glucose ratio]

(run number)

The data indicate that, for a fixed level of catalyst, lowering the co-catalyst level decreased the conversion. In all cases the selectivity to C_2 - C_3 material was 100%.

In run 88-B a 8.3% yield was obtained with a $Ca(OH)_2$/glucose ratio of 5/1. Under similar experimental conditions, run 88-A, a 2.5/1 ratio gave a yield of 17.3%. The Formose Reaction catalyst probably consists of a complex of $Ca(OH)_2$ and glucose. Thus, increasing the $Ca(OH)_2$ to glucose ratio would decrease the concentration of such a complex and thus reduce the CH_2O conversion level.

4. Study of the Role of the Co-Catalyst in the Formaldehyde Condensation System

In order to develop an understanding of the role that the co-catalyst performs in the HCHO condensation reaction, we studied what happens to the co-catalyst itself, in the presence of $Ca(OH)_2$ alone. Formaldehyde was not present in this series of runs. Glucose, Mannose, Fructose, Galactose and Arabinose were subjected to this treatment at the 0.0018 m level with $Ca(OH)_2$ at the 0.009 m level at 60°C for 10 minutes. Preliminary results indicate that cleavage occurs along with epimerization and isomerization.

	Glucose	Fructose	Mannose	Galactose	Arabinose
% Sugars Recovered	100 (76-15)	28.5 (76-17)	88.3 (76-16)	85.6 (76-18)	(76-19)
Analysis G C Curve	C to C_2+C_3 E + I to other C_6 (Fructose Some C_4 + C_5 present.	C to C_2+C_3 E + I to other C_6 (+ Glucose Some C_4 + C_5 present.	C to C_2+C_3 E + I to other C_6 Some C_4 + present.	C to C_2+C_3 E + I to other C_6 Some C_4 + present.	C to C_2+C_3 E + I to C_5 Some C_6 present.

Sugar 0.0018 m
$Ca(OH)_2$ 0.009 m
10 minutes
60°C

C = Cleavage
E = Epimerization
I = Isomerization
(run number)

The low percent of sugar recovered from the Fructose is probably an indication of the extent of cleavage to low molecular weight materials.

C. Homogeneous Flow Reactor Studies

Studies were carried out in a homogeneous flow reactor similar to that used by Mitchell (8). Flow reactors are more advantageous because they allow one to closely control the time that the reactants are in contact with the catalyst at elevated temperatures. This reaction technique was used to produce large quantities of formoses relatively free of caramel. The latter is rather easily formed when the formose mixtures are exposed to high temperatures for any substantial period of time. In the first run, where we used a five meter reactor, the product was overcooked during the rotary film evaporation. Up until the evaporative step it looked quite light in color. Because of this, the temperature of the bath used with the rotary evaporator was reduced to 50°C or less. Table III summarizes the runs carried out in the 5 meter Tygon tubing helix reactor and in a 10 meter helix reactor constructed to increase the throughput by increasing the flow rate of formaldehyde concentration from 4 to 8%. Several homogeneous catalysts were also studied, as well as several co-catalysts.

A comparison of Runs 6 and 7 shows that an increase in the concentration of formaldehyde and a decrease in the residence time reduced the conversion. Increasing the $Ca(OH)_2$ concentration (run 8 versus 9) al o increased the conversion to sugars. Use of $Ca(OH)_2$ yields exceedingly low color products; in several cases (Runs 9, 11, 13) pure water white crystal clear syrups and white crystals* (Runs 11, 13) were obtained. Use of catalysts other than $Ca(OH)_2$ (i.e., $Mg(OH)_2$ and $Th(OH)_4$) resulted in large quantities of the formaldehyde being converted to paraformaldehyde. With $Mg(OH)_2$, a temperature increase of 20° had a greater effect on the yield of sugars than a twofold increase in the catalyst level. Runs 9, 11, and 13 were essentially the same except for the fact the product from Run 13 was deionized by an ion exchange resen. White crystals were obtained in Run 13 when the product mixture was allowed to stand for an extended period of time.

The data show our clean, white, non-caramellized reaction products to be extremely complex as was the case with the batch type reactions. However, an examination of the G.C.'s from runs 9, 11 and 13 (which are similar enough to be considered as replicates) indicate a marked selectivity to low molecular weight C_2 and C_3 products with none or only trace quantities of compounds in higher molecular weight ranges.

One difference in experimental procedure with these runs compared to other early exploratory runs was the fact that 9, 11 and 13 were quenched by adding solid CO_2 immediately to the reaction mixture at the end of the 9-14 minute contact time. Therefore, we believe that quenching with carbon dioxide helped to prevent further condensation to complex mixtures, presumably by removing excess calcium as $CaCO_3$.

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*The crystals from #11 did not melt up to 260°C, but they did char and caramellize. They gave the odor of burning sugar.

III. STUDIES OF THE FORMALDEHYDE CONDENSATION REACTION IN A HETEROGENEOUS SYSTEM

A. Exploratory Catalysis Studies

A series of heterogeneous catalytic studies were made in our flow reactor system. First, catalyst screening studies were made in which the metal oxide type, support and homogeneous co-catalyst type were varied. A number of alkaline earth oxides supported on alumina were tried. Alumina was chosen because it has been successfully used in many catalytic applications. Using calcium oxide, supports other than alumina were tried including silica. Various "co-catalysts" were also tried to determine if they had any effect on the distribution of sugar products as well as to see if they increased the conversion of formaldehyde. Their effect on the ratio of sugar to paraformaldehyde was also of interest. An effort was initiated to study the stability of the catalysts used during an extended reaction period. Since evidence indicated that calcium oxide was being lost from our early catalysts, a series of modifications in the preparation procedure were made and a catalyst pre-treatment procedure was investigated.

All of the studies made in the heterogeneous flow reactor are summarized in Table IV and the pertinent G.C. curves are appended to the Table. The runs are arranged in this Table to emphasize relationships, so they are not in chronological order (the order of the notebook pages). The corresponding G.C. curves, which follow, are numbered in accordance with the Table for convenience of cross-reference. Table VIII summarizes the catalysts and their preparation.

In these heterogeneous runs formaldehyde formed paraform under acid conditions (whenever the effluent pH is below 7). This formation of paraform did not occur in our homogeneous runs, and as a result a more complex analytical procedure had to be used with our heterogeneous runs. Where the yield of sugar was appreciable, the paraformaldehyde did not interfere in the G.C. determinations of the TMS derivatives of the sugars. Hemi-formals which were also formed increased the complexity of the curve, since each hemi-formal formed a TMS derivative with a higher retention time than that of the parent sugar. Since the hemi-formal TMS derivative possessed one less hydroxymethyl group, it did not have a retention time in the region of those of the next higher sugars. Thus a complex curve with many peaks formed. In many cases, the amount of sugar formed was so low compared to the paraform that no curve could be obtained. Evaporation of the paraform on a Steam Bath or in a Vacuum Oven was necessary to obtain enough sugar for G.C. curves. This evaporation was also necessary to determine the yield of sugars as well as the relative amount of paraform. Use of a micro determination with 100 milligrams of product on a Fisher-Johns melting-point Apparatus demonstrated close agreement with the two micro-methods. However, losses of glyceraldehyde and dihydroxyacetone were large (over 50%) when pure samples were checked by the micro-method. For this reason, where possible,

G.C. curves were run on both the evaporated sugars and on the mixture of paraform and sugars as it was obtained from the effluent. This would help us to avoid missing the C_3 and C_2 compounds if they made up an appreciable portion of the product. See the G.C. curves for Runs 22 (Figure 48), 24 (Figure 50) and 25 for comparisons. In some cases evaporation of the paraform also simplified the curve, reducing the peaks. Compare Figure 83 and 84 for an example of a great simplification of the curve brought about by loss of the paraform. Products from Run 17 and 28 have an extremely regular pattern in the G.C. with few peaks. Since these had only traces of sugars at best, the peaks must be those of TMS derivatives of members of the $HO(CH_2O-)_nH$ series (n = 1,2,3,4...). In many cases, where there are low concentrations of sugars, evaporation of the paraform allows TMS peaks to appear, although they are unseen in G.C. curves of the original mixture.

A series of catalysts containing different alkaline earth oxides and rare earth oxides supported on alumina were prepared by a straight-forward impregnation technique. These include catalysts FC-1 to -5. Tests of these catalysts indicated that CaO was preferred to the other oxides tested. This result, of course, confirms previous experience in homogeneous reaction studies. Alumina itself (Runs 1 and 2) yielded low quantities of sugars and a high yield of paraform. This result suggested that other substrates should be looked at. The catalyst preparation procedure was also modified, including more quantitative impregnation techniques and the use of higher calcination temperature (i.e., 1500°F). In this later modification, it was hoped that a higher calcination temperature would aid the calcium cation to penetrate the alumina lattice and thus be more strongly bound to the substrate. Such procedures have been used to "dope" semi-conductors with a foreign cation, but have the disadvantage of greatly reducing catalyst surface area because the high temperatures necessary to "open" the crystal lattice markedly accelerate sintering of the material. Tests of two supported calcium catalysts prepared in this manner, (FC-6 and FC-13 which were used in runs 19-22 and 23-25) demonstrated that in a fresh catalyst, such a modification increased the sugar content and decreased the paraform content (19 and 23). As they were used in further runs, paraform tended to increase relative to the sugar and the sugar yield itself dropped. In these runs an effect of the co-catalyst type was observed and will be discussed later. Results of these experiments are summarized below:

Catalyst Age	Conversion and selectivity[a]	Catalyst	
		CaO/SiO$_2$ FC-6)	CaO/Al$_2$O$_3$ (FC-13)
Fresh (Runs 19 and 23)	Conversion to sugars	37%	61.4%
	% C$_3$ (Monomer and dimer)	8.7[b]	11.1%[b]
Used (Runs 22 and 25)	Conversion to sugars	14.2%	20.2%
	% C$_3$ (monomer and dimer)	6.2	35.3%[b]

(a) Test conditions: 60°C, 0.27 W/hr/W (gCH$_2$O/hr/g cat.), glucose co-catalyst.

(b) Analysis of non-evaporated sample.

It can be seen that both the CaO/SiO$_2$ and the CaO/Al$_2$O$_3$ catalyst deactivated with use. On both a fresh or used basis the CaO/Al$_2$O$_3$ catalyst is superior to CaO/SiO$_2$. It is also very interesting to note that the used CaO/Al$_2$O$_3$ catalyst exhibited a marked improvement in selectivity. This result seems to parallel our experience in our homogeneous studies which indicates that the key to improved selectivity is proper control of catalyst activity. More important, these results demonstrate that improved selectivity to the desired glyceraldehyde and dihydroxyacetone can be achieved in a heterogeneous reaction system as well as a homogeneous reaction system.

Homogeneous runs 9, 11 and 13 and heterogeneous run 25 clearly show that the glucose co-catalyst is capable of being converted to other compounds in an active reaction system. Thus, it is reasonable to expect marked effects of co-catalyst type. In this respect, C$_6$ sugars, which presumedly undergo such a redistribution, such as glucose and fructose, seem to give enhanced yields with active catalysts and tend to decrease the conversion to paraform while the C$_5$ sugars, D-Xylose and L-Arabinose, which may not break down as readily, do not give high yields. Glyceraldehyde appears to give a moderate yield although it was tested only once and then with a poor catalyst, FC-3. Sorbitol and Mannitol, which are not capable of forming enediols, do not show desirable co-catalyst activity (Runs 9, 13 14 and 18 in Table IV).

B. Fundamental Studies of the Formaldehyde Condensation
    Reaction in a Heterogeneous System

A number of studies involving formaldehyde condensation with heterogeneous catalysts were made. This work included studies of the effect of changing co-catalyst type, extended runs with a given catalyst to pin down conversion and selectivity changes as a function of catalyst life and screening runs with new catalyst preparations.

1. Study of the Effect of Co-Catalyst Type

Previous work has established that the use of glucose as a co-catalyst is beneficial in both the homogeneous and heterogeneous condensation reaction system. However, it is more advantageous in an actual space-craft application to recycle part of the product C$_3$ sugars to the condensation reactor, rather than to carry glucose on-board the craft. Thus we have investigated if a C$_3$ sugar, i.e., glyceraldehyde, could be substituted for glucose as the co-catalyst in our heterogeneous condensation system. These experiments were carried out by changing co-catalyst type in several of our extended catalyst runs. Detailed results are shown in Table V. The effect of co-catalyst type on the % CH$_2$O converted to sugars is summarized below:

Catalyst	Runs	% Conversion To Sugars[a]	
		Glucose	Glyceraldehyde
Impregnated CaO/Al$_2$O$_3$	47,46	38.6	70.8
Co-precipitated CaO/Al$_2$O$_3$	36,37	12.5	19.1
La$_2$O$_3$/Al$_2$O$_3$	33,35	6.8	19.1
Ce$_2$O$_3$/Al$_2$O$_3$	39,40	10.5	9.8

(a) Other conditions: 60°C, 0.27 W/Hr/W in units of grams CH$_2$O per hour per gram of catalyst, 10 grams of co-catalyst.

It can be seen that with the CaO/Al_2O_3 and La_2O_3/Al_2O_3 catalysts the use of glyceraldehyde increased the conversion to sugars. In all these cases the selectivity to C_2 and C_3 sugars was good, in some cases the G.C. analyses indicating all $C_2 - C_3$ sugar. With the Ce_2O_3/Al_2O_3 catalyst no effect of co-catalyst type was observed. The conversion level with this catalyst was also quite low. Most important, however, is the high conversion level (i.e., 70%) and good selectivity achieved with glyceraldehyde as a co-catalyst using a CaO/Al_2O_3 catalyst (run 46). Interestingly enough, this good selectivity achieved with glyceraldehyde with a heterogeneous calcium catalyst is in contrast to our experience with homogeneous systems, where the use of glyceraldehyde as co-catalyst resulted in poor selectivity to lower sugars. In other studies where the glyceraldehyde alone was put through a catalyst bed, (Ce_2O_3/Al_2O_3) (run 41) with no formaldehyde present, only $C_2 - C_3$ sugars were obtained; no condensation to higher sugars occurred. Use of fructose and glucose as co-catalyst seemed to be about equivalent to each other with a CaO/Al_2O_3) catalyst. Use of mannose (run 32) with an extensively deactivated catalyst (CaO/Al_2O_3) raised the sugar yield to 25% versus 13% with glucose and maintained the product selectivity to the $C_2 - C_3$ products. Putting glucose without formaldehyde through a fresh CaO/Al_2O_3 catalyst had yielded a brown syrup with some $C_2 - C_3$ product present; but mostly epimerized C_6 sugars were present.

Two recycle trials using product sugars from 387-13f, and 387-11f, (runs 38 and 48 respectively) were not very promising. However, these materials may be unusual since they were prepared in homogeneous reactions and they may be in the form of condensed formals.

2. Screening of Other Heterogeneous
   Metal Oxide Catalysts

In addition to CaO/Al_2O_3 catalysts, a number of other catalysts were also screened. La_2O_3/Al_2O_3 and Ce_2O_3/Al_2O_3 yielded low yields of sugars, as indicated previously. Use of glyceraldehyde instead of glucose with the Ce_2O_3/Al_2O_3 catalysts did not improve the conversion to sugars. Test of a CaO/silicate preparation (run 42) indicated that this catalyst was inferior to the CaO/Al_2O_3 catalyst. Tests of a PbO/Al_2O_3 catalyst show that this catalyst has good activity for the condensation of CH_2O to sugars, and with glyceraldehyde as the co-catalyst also showed good selectivity to $C_2 - C_3$ sugars.

Two runs (runs 28 and 35) were also made in which the space velocity, i.e., (W/Hr/W), of the reaction system was varied. As would be expected, increasing the contact time by lowering the W/Hr/W increased the conversion level, while decreasing the contact time by increasing the W/Hr/W lowered the conversion level.

Since the PbO/Al_2O_3 catalyst showed good activity, 30-50% conversion, for the condensation of HCHO to sugars with good selectivity to $C_2 - C_3$ material. Therefore, we looked at the ability of other metal oxides, namely CoO, CuO, NiO, ZnO and Fe_2O_3, supported on Al_2O_3 to function as HCHO condensation catalysts.

The catalysts were prepared by impregnating Al_2O_3 pellets with a solution of the soluble salt of the desired metal, followed by calcination to obtain the supported metal oxide.

The catalysts were screened in our heterogeneous flow reactor at 60°C, space velocity 0.27 w/hr/w, using 9% aqueous HCHO + 1 mole % co-catalyst. Glyceraldehyde, mannose and glucose were used as co-catalysts in consecutive runs. The catalysts were not pretreated in any of these studies.

Cobalt oxide on Al_2O_3 (FC-19) with glyceraldehyde gave 11.5% conversion with high selectivity to $C_2 - C_3$ material. Conversion decreased to 6.7% with mannose and then to 7.4% with glucose. The selectivity to $C_2 - C_3$ material decreased using the C_6 sugars as co-catalysts. Catalyst leaching was also a problem in all three runs. Therefore CoO/Al_2O_3 is not an attractive HCHO condensation because of its low conversion and the leaching problem.

Nickel oxide on Al_2O_3 (FC-17) produced about the same results as CoO/Al_2O_3. Glyceraldehyde gave a 9.3% conversion, mannose gave a 8.8% conversion and glucose gave 7.8% conversion. Good selectivity was present with glyceraldehyde but was decreased with the other co-catalysts. The leaching problem was also present.

Copper oxide on Al_2O_3 (FC-18) with glyceraldehyde, mannose and glucose gave conversions of 5.7%, 8.3% and 8.4% respectively. Selectivity also decreased with use of glucose as with the other metal oxide catalysts. Catalyst leaching also occurred.

Zinc oxide on Al_2O_3 (FC-20) with glyceraldehyde gave 18.4% conversion with high selectivity. Subsequent use of mannose and glucose gave decreased conversions (6.9% and 6.7%). Selectivity was maintained with mannose, but decreased with glucose. ZnO leaching was not analyzed.

Iron oxide on Al_2O_3 (FC-16) produced quite high conversion levels. Screening was carried out using only glyceraldehyde as co-catalyst in consecutive runs. The first run gave a 49.7% conversion. Run 2 gave 97.8% conversion. Run 3 gave 44.7% conversion. Iron oxide has been reported in the literature to be an effective homogeneous HCHO condensation catalyst. Therefore, an iron oxide catalyst is attractive for our use as an HCHO condensation catalyst. Leaching of this catalyst also seemed to be a problem. The presence of Fe^{+++} was confirmed by use of the potassium thiocyanate test. Acetic acid was added to break up the iron complexes. The quantity of iron present in the reactor effluent progressively decreased with each consecutive run. These results are highly encouraging and indicate that iron oxide and calcium oxide catalysts are both attractive for the formaldehyde condensation reaction. Of special note is the fact that human metabolism can tolerate any leached Ca or Fe that would accompany the synthesized glycerol.

3. Study of Ion Exchange Resins as Catalysts
    and Catalyst Supports

Ion exchange resins were screened for use as possible catalyst supports as means of preventing the leaching of the metal ion off the support. Strongly acidic, weakly acidic, strongly basic and weakly basic type resins were used. The catalysts were prepared "in situ" by saturating the resin bed with a salt solution. Non-exchanged resin were also tested. The data are summarized in Table IX of the Appendix.

Amberlyst 15 (RFC-3), a strongly acidic non-exchanged resin without co-catalyst, gave zero conversion to sugars. Subsequent runs using glucose and glyceraldehyde co-catalysts gave 7.2 - 8% conversions. Ca^{++} saturated amberlyst 15 (RFC-5) in the absence of co-catalyst also was not active. In the presence of co-catalysts, sugar yields of 7.2 - 12.5% were obtained.

Lead saturated amberlyst 15 (RFC-6) even without co-catalyst gave 9% sugars, while with co-catalysts it gave a 21 - 21.5% yield. This indicates that lead is a useful catalyst which was definitely shown by the high yield given by the FC-15 PbO/Al_2O_3 catalyst previously used. This catalyst yielded 53% of a predominately $C_2 - C_3$ sugar mix. Use of a lead based catalyst, however, represents a potential toxic hazard.

An iron exchanged strongly acidic resin (IR-120) catalyst, RFC-11 using glyceraldehyde as a co-catalyst only gave a 12.6% yield. This is not as attractive as the FC-16 Fe_2O_3/Al_2O_3 catalyst.

Two strongly basic resins were screened for their catalytic activity. RFC-3, Amberlite IRN-78 in the absence of co-catalyst gave zero conversion and with co-catalyst gave 8.8 - 10.5% conversion. RFC-9, OH-exchanged form of IRA-401S gave similar conversions.

Am'erlite IR4B, a weakly basic resin, gave 1.9% conversion in the absence of co-catalyst. The use of glucose co-catalyst gave a 6.5% conversion. When glyceraldehyde was used as a co-catalyst the yield increased to 17.6%.

Thus, ion exchange resins do not seem to be particularly attractive as catalyst supports.

4. Study of Calcium and Iron Containing
    Molecular Sieves as Catalysts

Calcium and iron forms of molecular sieves were screened as possible catalysts for the condensation of formaldehyde. Previous work with these metal ions indicated good catalytic activity and incorporating them into the zeolite structure could lead to a stable catalyst with calcium and iron in a non-chelatable form.

A commercially available Ca^{++} exchanged sieve, Linde 5A, was tested using glyceraldehyde co-catalyst at 60°C. Two consecutive runs gave conversions of 19.8 and 15.2% respectively. Fe^{++} sieve was obtained by exchanging 13X sieve with $FeCl_2$ solution. When this catalyst was run with glyceraldehyde as co-catalyst, 10.6% conversion was obtained. No catalyst leaching was observed with either catalyst. However, the low conversion obtained does not make molecular sieves attractive as formaldehyde condensation catalysts.

5. Catalyst Activity and Selectivity Maintenance in an Extended Run

Catalyst performance for an extended period of time is required for a successful spacecraft application. Thus, an extended study of the stability of a CaO/Al_2O_3 catalyst, (which had been calcined at 1500°F) was made. The catalyst was first subjected to an extended water wash until the effluent wash water reached a constant pH value. The catalyst lost about 10% of its CaO during this leaching. Then an extended run was made using a 9% formaldehyde solution containing 1 mol % of glucose at 60°C with 500 ml cuts of effluent being taken (run 32). Each was worked up independently. Conversion of CH_2O to sugars remained essentially constant. The selectivity to $C_2 - C_3$ sugars exhibited a complex pattern. The first product samples showed good selectivity to $C_2 - C_3$ sugars, further samples showed increasing amounts of higher sugars, and the final sample again showed a selective $C_2 - C_3$ product. Chemical analysis of the fresh and spent catalyst indicated that the calcium content of the catalyst fell from 16 wt% to 0.9 wt% CaO (after run 38). Thus, the catalyst underwent extensive leaching of the calcium throughout this extended run.

In an attempt to minimize this calcium leaching problem in runs 51 through 54 the FC-13B catalyst was pre-leached in run (51), with a very high glucose solution. This pre-leached catalyst was then employed in a standard 9% formaldehyde solution run. As can be seen, this catalyst, gave a high yield of sugars and was also selective toward $C_2 - C_3$ sugars.

The PbO/Al_2O_3 catalyst (FC-15) was re-run to verify the high conversions and selectivity obtained previously. A series of consecutive runs were made using this catalyst with the standard 9% HCHO solution employing glucose as the co-catalyst. The conversion obtained after the first run was 39.9%, maintained at ɔ1.2% after the second run and was drastically lowered to 4.6% after the third run.

A similar series of consecutive runs were made using glyceraldehydr as the co-catalyst. The conversions obtained were 49.5, 33.9 and 33.5% respectively.

This indicates that glucose has a much stronger ability to complex with the PbO and deactivate the catalyst. Therefore, glyceraldehyde is a better co-catalyst for activity maintenance than glucose.

A CaO/Al_2O_3 catalyst (FC-13B) was subjected to a pre-treatment with a concentrated glucose solution. The object of this pretreatment was to stabilize the catalyst and minimize the calcium leaching problem during consecutive runs. The pre-leached catalyst was then employed in a series of runs using 9% aqueous formaldehyde and glyceraldehyde as co-catalyst. Four consecutive runs were made over the same catalyst bed. Conversion to sugars were 17.9, 24.2, 14.8 and 10.9% respectively. The selectivity was poor giving a wide range of products.

In a previously reported similar run (387-111, 113 and 115) the yields were much higher and much more selective.

The data from the two runs using pre-leached CaO/Al_2O_3 catalyst further illustrates the complexity of the leaching problem. The strong tendency of glucose to complex with the CaO deactivates the catalyst. This is in agreement with the data form the PbO catalyst.

Glyceraldehyde rather than glucose is preferred since it is a better co-catalyst for activity maintenance than glucose. From a practical standpoint this is highly favorable, for it demonstrates the feasibility of using a re-cycle stream as the co-catalyst.

IV. FUNDAMENTAL INVESTIGATION OF THE CATALYTIC HYDROGENATION OF THE FORMALDEHYDE CONDENSATION REACTION PRODUCTS

An investigation of catalysts and conditions for the hydrogenation of glyceraldehyde to glycerol was undertaken. Laboratory screening work was carried out in a batch reactor. This data can then be used to design a flow hydrogenation unit for the actual process application. The conditions have been set at limits which appear practical for spacecraft use, i.e., 100 lbs/in^2 hydrogen pressure and low temperatures. Most of the hydrogenation study have been confined to 60 lbs pressure (5 atm.) and temperatures of 115°C or below. The equipment used has been a Parr Hydrogenator.

A. Related Work in the Literature

In general, the major problem with aldehydes and particularly hydroxyaldehydes, according to the literature, has been their tendency to poison or destroy the catalytic activity of the catalyst by condensing as polymer on it. Most reductions of this type have been at substantially higher hydrogen pressures than those we can consider. Skinner(9) produces glycerol from glyceraldehyde in water in good yield by use of a Chrome-Raney nickel catalyst at 900 psig of hydrogen. In this patent, Skinner mentions the difficulty of prolonging the catalyst's life. He maintains the catalyst life by using quite dilute solutions of glyceraldehyde (14%). Adkins has reduced glucose over Ni on Kieselguhr but at a higher pressure(10). Reference (10) also states that use of active Raney nickel or noble metals allows reduction of aldehydes at lower pressures (1-3 atmospheres).

B. Preliminary Evaluation of Noble Metals and Raney Nickel Catalysts

Several trials were made with Noble metal and Raney nickel catalysts to hydrogenate glyceraldehyde as a model compound and also to hydrogenate an actual C_2 - C_3 product mixtures. In these tests all of the noble metals were ineffectual at ambient temperatures, including 5% Pd on charcoal, PtO_2, 5% Pt on charcoal, PtO_2 plus Fe^{+++}, $RuCl_3$ and 5% Ru on carbon. However, use of a stabilized Raney nickel catalyst led to a slow hydrogenation of the glyceraldehyde and a freshly prepared W-2 Raney nickel led to a quantitative take-up of hydrogen by the glyceraldehyde. A sample of the syrup, 387-13f$_1$, which on GC analysis was exclusively C_2 - C_3 components (with some formaldehyde present) was then hydrogenated using the fresh W-2 Raney nickel. Uptake of hydrogen was only about 50% of that expected. The mixture obtained was filtered and distilled under vacuum. A volume of viscous liquid resulted when the water had been removed. A green coloration indicated that some nickel was dissolved in the glycol-glycerol mixture. Extensive treatment with H_2S, several types of ion exchange resins and successive evaporation

and re-dissolving did not remove the dissolved nickel. On subjecting this mixture to higher vacuum and higher temperatures, we obtained evidence of distillation at the expected boiling point for glycerol and no evidence of glycol. However, a rapid carbonization of the pot residue occurred. Apparently the dissolved nickel caused decomposition or there were unreduced sugars present which polymerized. The GC of the TMS derivative of this residue showed peaks, one of which corresponds to glycerol.

A similar distillation with glyceraldehyde which had been reduced using 60 psig of hydrogen and W-2 Raney nickel yielded about theory of distillate with a small amount of pot char. This distillate on GC analysis of its TMS derivatives had two large peaks in the glycerol region and many smaller peaks throughout the curve. Apparently the W-2 Raney nickel is causing some condensation of the commercial glyceraldehyde during the hydrogenation. The hydrogenation, as seems true of all of those studied, was very slow, requiring 24 hours.

A second sample of product sugars from run 387-13f, was treated with hydrogen using Ruthenium on carbon and a ml of 12N HCl (recommended by a large noble metal catalyst company for this work). No hydrogen was absorbed after 22 hours at ambient temperature and the Ru on carbon was filtered off. Platinum oxide (0.5g) was added and the mixture treated with hydrogen at 60 psig for 22 hours. Finally, 0.5g of W-2 Raney nickel was added (without removal of the platinum). Over a period of 46 hours this mixture absorbed the theoretical amount of hydrogen for complete hydrogenation.

Treatment of 387-11f$_1$, a C_2 - C_3 mixture similar to 387-13f, but not freed of calcium, with 60 psig of hydrogen with W-2 Raney Nickel for 18 hours resulted in an uptake of 4.0 lbs of hydrogen pressure. PtO$_2$ was added and the treatment continued for 3 days longer with a further uptake of 1.8 lbs. The total, 5.8 lbs, is about 1/3 p.p. of theoretical hydrogen consumption.

Thus at room temperature only the use of platinum in conjunction with a nickel catalyst appeared to result in an active hydrogenation catalyst system. It is well known that platinum will dissociate molecular hydrogen into atomic hydrogen. Extensive studies with bifunctional catalysts have shown that such hydrogen is capable of migrating on a catalysts surface. Thus, it is reasonable to conclude that the function of the platinum in the mixed hydrogenation catalyst system is to provide atomic hydrogen which prevents an irreversible deactivation of the active nickel catalyst.

The effect of solvent on chelation of nickel during hydrogenation with bifunctional catalysts was studied. Methanol, presumed to be available on the spacecraft, was tested for use as solvent. Attempts to

reduce 387-111f$_1$ in methanol using PtO$_2$ and in combination with Raney Nickel gave only 1/3 of the theoretical hydrogen consumption. Therefore, methanol is not a suitable solvent for reductions with platinum - Raney Nickel catalysts. Use of methanol may require a different catalyst system.

Nickel, however, is a known carcinogen. Thus, because of tendency of nickel to chelate with the reaction mixture, its use in a practical glycerol does not seem possible.

C. Further Studies Using Noble Metal Catalysts

The chelating properties of glycerol toward nickel under the conditions of low temperature and pressure do not make the nickel-platinum system feasible. Therefore, we looked more extensively at the possibility of using noble metal catalysts at temperatures other than ambient.

Glyceraldehyde was used as substrate. A 5% Pt/Al$_2$O$_3$, catalyst gave no hydrogen uptake at a temperature of 70-80°C. Adam's Catalyst gave the same result at 95-100°C. A 0.5% Ru/Al$_2$O$_3$ catalyst gave no hydrogen uptake at 95°C. A massively loaded Iridium catalyst (30-35% Ir/Al$_2$O$_3$) was also unreactive.

A 5% Ru/C catalyst was found to be an effective catalyst for the hydrogenation of a glyceraldehyde solution. However, the reaction proceeded only when the temperature was raised above room temperature. A study of the reaction variables was undertaken with respect to temperature, pressure, substrate concentration and catalyst concentration.

In all runs, an induction period was present. The length of this induction period varied as other reaction parameters were varied. This data is summarized in Table X.

The effect of catalyst concentration on hydrogen uptake was studied. Three catalyst levels (1, 2, and 5 gm) were used keeping pressure, temperature to substrate concentration constant. The length of the induction period decreased with increasing catalyst concentration. The rate of hydrogen uptake increased somewhat as the catalyst loading increased from the 1 to 2 gram level. However, a synergistic effect was noted for 5 gm level (Figure 165) as the hydrogenation rate increased markedly.

The effect of pressure on hydrogen uptake was studied at 30 and 60 psig. The rates of hydrogen uptake (Figure 166) at 30 psig appears to be faster than at 60 psig, however, the number of moles of H$_2$ in the system at 30 psig is 1/2 that at 60 psig. Therefore, the rates are about the same, making the rate of hydrogen uptake independent of pressure.

The effect of glyceraldehyde concentration was studied at the 20 and 40 gm level (8.1 and 12.8 wt.% respectively). As shown in Figure 167 the rate of hydrogen uptake is dependent on glyceraldehyde concentration. An examination of the data indicates that the rate of hydrogenation is first order in glyceraldehyde concentration.

The effect of temperature on rate of hydrogen uptake was studied at two temperatures. The initial slope of the curve was approximately the same in both runs, but the overall rate at 87°C temperature appears to be greater than that at 115°C Figure 168). Previous data indicated that the rate was very slow at ambient temperature. Thus, an optimum temperature range for hydrogenation exists.

D. Chemical Methods of Reduction

The use of sodium borohydride, $NaBH_4$, for the reduction of sugars is well documented in the literature(11,12).

Sodium borohydride easily reduced 387-13f$_1$ glyceraldehyde (from formaldehyde condensation). However, in the work-up only a small amount of reduced sugars was obtained on evaporation of the solution. Apparently most of the sugars were being held on the ion exchange resins as the borate complex. The small sample, which we obtained, on treatment with Tri-Sil and separation in the G-C showed a large peak in the glycerol region accompanied by many other lesser peaks. This partially confirms the G.C. curve on 387-13f$_1$ which indicated a preponderance of glyceraldehyde.

A parallel reduction on 387-111f$_1$ with sodium borohydride was run. This reduction product was rendered strongly basic to saponify the borate esters. Attempts to extract glycerol with ether and t-butanol were unsuccessful.

Chemical reduction is not feasible since all reducing agents would have to be brought on the mission. We have successfully using chemical reduction to confirm the presence of C_3 material in our product samples.

V. STUDIES OF SEPARATION PROCESSES

No detailed work was done initially on separation processes for our two step process because at that time the nature of the process to be employed was not defined. After the process was more clearly deliniated, preliminary studies of separation techniques were made.

A. Separation and Recovery of
    Complexed Catalysts

Consideration of separation processes should consider possible means to separate and recover chelate complexes from the effluent of both process steps.

The literature indicates a method of separation employing an ion exchange resin described in a patent by MacLean and Stautzenberger(13). The polyvalent metal compound catalyst is removed from the carbohydrate mixture by any of several methods. In the preferred method the carbohydrate reaction mixture is passed over an acidic cation-exchange resin, such as a phenol sulfonic acid-formaldehyde reaction product or a sulfonated styrene-divinyl benzene copolymer, such resins being exemplified by Rohm and Haas Amberlite IR 120. This effects the removal of the combined metal, such as lead, and also decreases the pH of the carbohydrate mixture, for example to a pH of 3.5 to 2.

The condensation catalyst must be completely removed, for its presence could cause further undesirable condensation reactions in the following stages of the process.

B. Removal and Recovery of
    Unconverted Formaldehyde

The unreacted formaldehyde must be removed from the sugar mixture prior to the reduction step. The presence of formaldehyde has caused catalyst surface fouling previously described in the Hydrogenation Section. Secondly, any unreacted formaldehyde entering into the hydrogenation reactor will consume hydrogen and be reduced to methanol.

MacLean(13) et al., describes a system for the separation of HCHO. The formaldehyde is preferably removed from the carbohydrate mixture by distillation at a pH of about 5 to 3. To insure adequate removal of the formaldehyde in the distillation step, the formaldehyde content of the mixture should not be over 5%. Where it is over 5% the mixture should be diluted with water to a formaldehyde content of 5% or less. The distillation may be carried out by introducing the mixture into the middle of a packed column, with or without column reflux and maintaining a base temperature of 102 to 105°C. If desired, the distillation may be carried out under pressure. The recovered HCHO is then recycled.

C. Separation and Purification of Glycerol
   from Hydrogenated Product Mixture

The purification of the final glycerol product is crucial since
the glycerol is to be used as a food. Vacuum distillation may be used
for purification. The boiling point range of the compounds in question
suggest that this separation is possible.

	B.P. (760 mm)
Ethylene Glycol	197°C
Propylene Glycol (1,3)	214°C
Glycerol	290°C
Erythritol	331°C

Glycerol is purified in glycerol containing mixtures by dis-
tillations at low temperatures and low pressures as reviewed by Baker(14).

VI. PROCESS DESIGN CONSIDERATIONS

Based on data presented in the previous sections of this report, a process for the production of glycerol has been identified and shown to be chemically feasible. This process employs formaldehyde as the starting material and is shown schematically in Figures 169, 170, and 171. The overall process consists of two chemical steps, first, selective self-condensation of formaldehyde to C_2 and C_3 sugars, and second, hydrogenation of the C_3 sugar product (glyceraldehyde and/or dihydroxyacetone) from stage I to glycerol. A separation step will be required in each step of the process, with recycle of the water solvent and other species such as unconverted feed materials. Based on these and other considerations, calculations were made of the amounts of materials that would be handled in the process.

A. Condensation Reactor System Calculations

It was assumed that the condensation reactor system consists of a bed containing CaO on Al_2O_3 catalyst maintained at 60°C and one atmosphere pressure. A formaldehyde plus co-catalyst solution is passed over the catalyst bed at a space velocity of 0.27 W/hr/W. It was assumed that a 60% conversion of formaldehyde to sugars is obtained with 95% selectivity to glyceraldehyde and dihydroxyacetone. In the separation step the C_3 sugars are separated from the C_2 sugars and unreacted HCHO which are recycled. The C_3 sugars are then fed into the Hydrogenation Reactor.

B. Hydrogenation Reactor System Calculations

It was assumed that the Hydrogenation Reactor System (Figure 171) consists of a bed containing 5% Ruthenium on carbon maintained at 85°C and 5 atm. The aqueous C_3+ fraction is passed over the bed, converting the glyceraldehyde and dihydroxyacetone to glycerol and any C_4^+ material to polyols. In a separation step the glycerol is recovered from water which is recycled and higher sugars which can be converted back to CO_2 and water.

Figure 169

Overall Schematic of Process for the Production of Glycerol
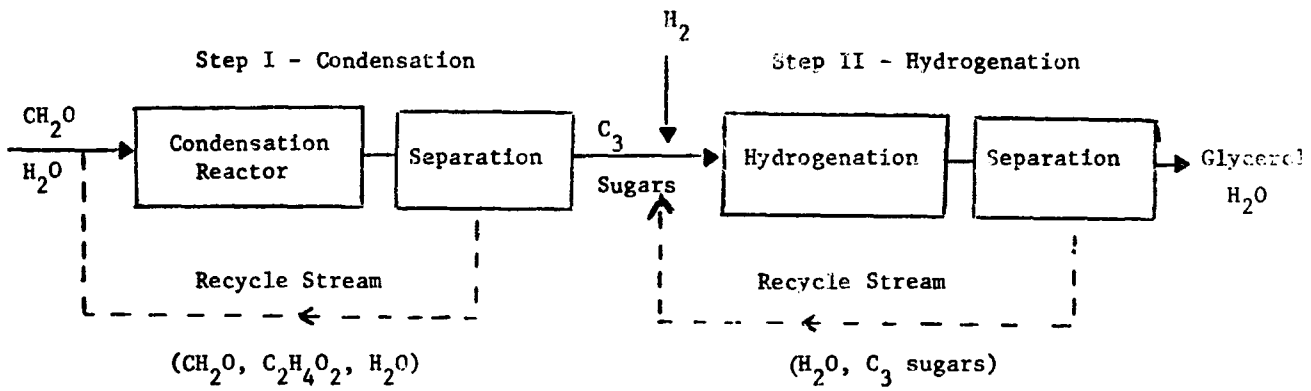
Figure 170

Condensation Reactor System

4,891 g/D CH$_2$O

41,409 g/D H$_2$O

Condensation Reactor → **Separation Step**

4,891 g/Day C$_3$ Sugars

49,409 g/Day H$_2$O

Recycle

3,260 g/D CH$_2$O

32,990 g/D H$_2$O

249 g/D C$_2$ Sugars
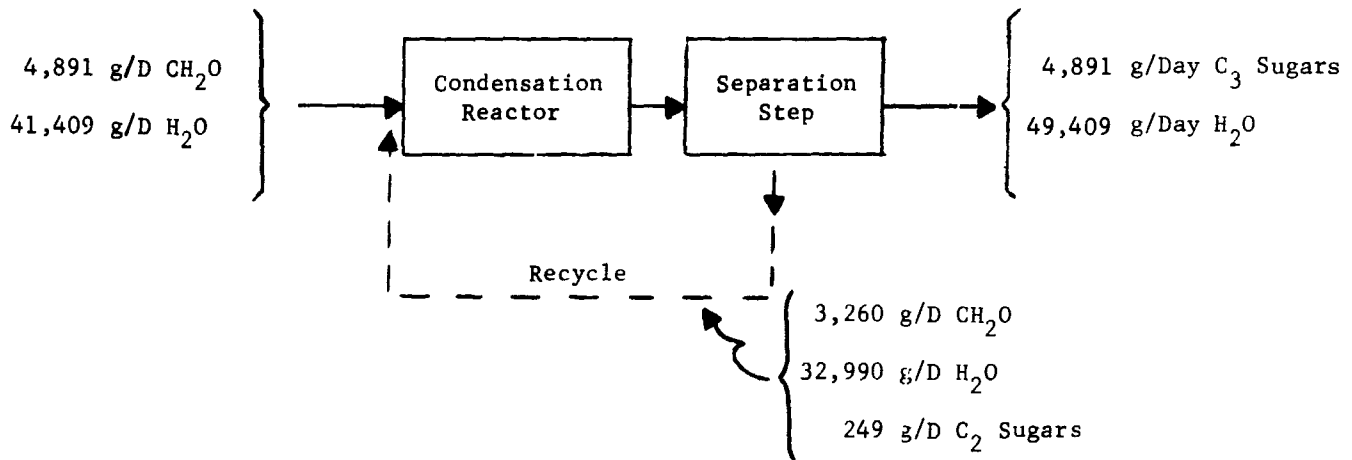
Conditions:
- 60°C
- CaO/Al$_2$O$_3$ Heterogeneous Catalyst
- 0.27 W/hr/W
- 1 atm total pressure
- 60% conversion of CH$_2$O to sugars
- 95% of sugars are glyceraldehyde and dihydroxyacetone
- Separation process assumed to remove 99% of C$_3$ sugars from recycle stream

Figure 171
Hydrogenation Reactor System

109 g/D H$_2$

H$_2$

4,89? g/D C$_3$ Sugars

49,409 g/D H$_2$O

Hydrogenation Reactor

Separation Step

5,000 g/Day Glycerol

49,409 g/Day H$_2$O

Recycle

50 g/D C$_3$ Sugars

505 g/D H$_2$O
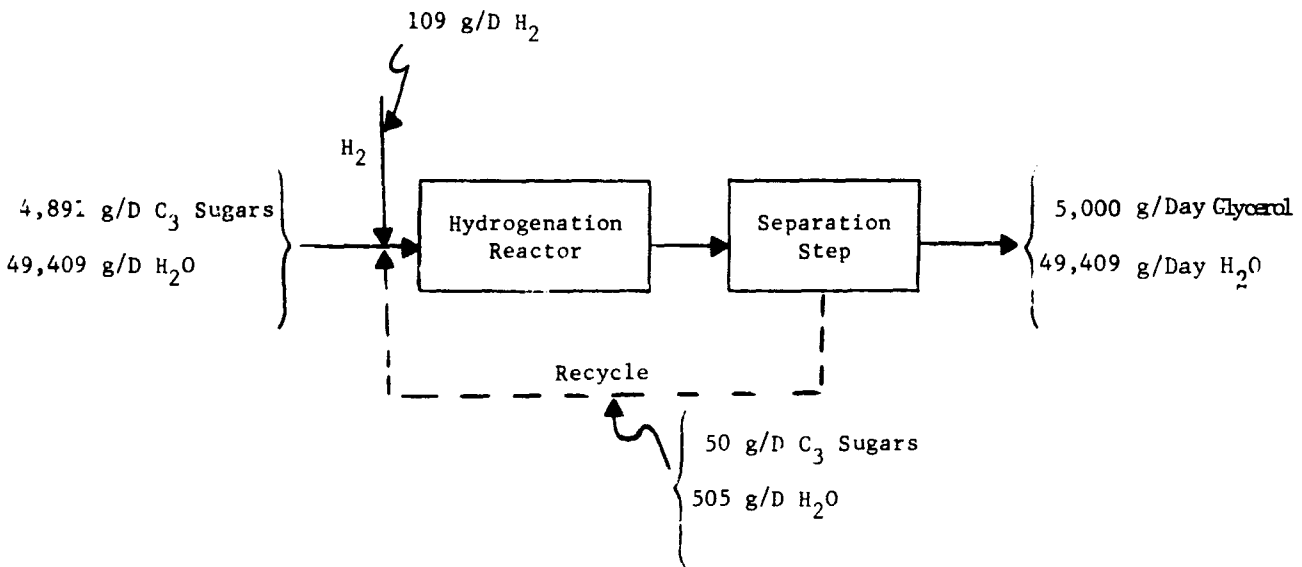
Conditions:
- 30°C
- 60 psig H$_2$
- Ru/E Heterogeneous Catalyst
- 99% hydrogenation of C$_3$ sugars to glycerol
- Assumed 99% removal of product glycerol from stream before recycle

VII. EXPERIMENTAL METHODS

A. Analytical Procedures

G.C. analyses were performed on a 6' S.S. 1/4" O.D. column packed with 3% SE-52 on chromosorb WAW DMCS as recommended by Sweeley(7). An F&M model 609 flame ionization detector unit equipped with a recorder was used. The column temperature was 75°C initial, programmed at a rate 2.5°/min to 155°C and then maintained at 155°C for the remainder of the analysis. Column inlet pressure was 30 psig with helium as a carrier.

A calibration, or standard, curve was obtained from TMS derivatized sugars purchased from Pierce Chemical Co., Rockford, Illinois, and TMS derivatized sugars converted from sugars obtained from other chemical supply houses. TRI-SIL DMF available from Pierce Chemical Co. was used to make the TMS derivatives of sugars and the products from the formaldehyde condensations reported in this Quarterly. One microliter samples were used for the curves unless larger samples were needed in marginal cases and to enlarge small peaks.

The G.C. curves obtained from our formaldehyde condensation reaction products were extremely complex, containing in some instances 60 components. We therefore adopted a standard interpretation proc_dure of dividing the curves into regions, the boundaries of which we defined by carbon number (C_2- C_3, C_4, C_5, $(C_3)_2$, C_6, $>C_6$). By comparing our calibration curve with these curves, we were able to pinpoint the various components of our reaction mixtures. Where a co-catalyst was used, its peaks and the area of its peak were not measured, thus emphasizing those sugars arising from the condensation reaction.

Retention values and boundaries used in our interpretations may be found in Table I. Glucose was used as the main reference retention value. Integration of the curves to obtain areas was done using a Fennel Maho-Planimeter.

At the present time we do not have any calibration standards for materials greater than C_6 sugars. This fraction is reported as "% greater than Glucose". Also the retention time for glycolaldehyde relative to glucose is not yet certain. Apparently it is similar to glyceraldehyde in forming a monomer and a dimer both of which show up in the G.C. curve. In our reported G.C. analyses we show C_3 and higher material. If C_2 monomer is present, it is probably being masked by the solvent peak. It is felt that a C_2 dimer would probably come out in the C_4 region. Thus, a note of caution must be appended to this discussion of the G.C. analysis of TMS sugar derivatives. These analyses and the percent composition determined by summation of areas refer only to C_3 and higher components which are volatile under the conditions used. Thus, this G.C. procedure is principally an invaluable tool to use for getting information on trends in the distribution of CH_2O condensation products.

B. Run Procedures.

1. Homogeneous Batch Reactor Studies

These small batch runs are carried out using a large constant temperature bath. The mixture of formaldehyde solution, water, and co-catalyst is immersed (in a 100-200 ml flask) in the bath and stirred by means of a magnetic stirrer. An inert atmosphere is maintained by a small stream of nitrogen in the neck of the flask. When the temperature of the mixture reaches that desired, the catalyst is dropped in and the timing begun. At the end of the desired time, the following treatments are used (as specified): cooling, quenching with CO_2, rapid filtration, standing to cool, evaporation of solvent, or various combinations. The small batch runs are usually organized as 2^n factorials to obtain the maximum information. Water used in the runs is usually heated on a Steam Bath under a stream of nitrogen to remove oxygen and transferred using pipettes to minimize oxygen uptake.

2. Homogeneous Flow Reactor Studies

The feed mixture was prepared in a large five liter flask equipped with an anchor stirrer which held the solution with its suspended catalyst. A tube which dipped into the bottom of the flask was connected to a rotary pump. This pumped the solution and suspended catalyst back into the flask. In the flow line, a small by-pass valve (adjustable) allowed delivery of a regulated flow of feed to the helix reactor held in a constant temperature bath. Flow was regulated to allow a controlled exposure time. The mixture was then allowed to cool. Dry ice was added to cool the mixture and neutrallize the catalyst. The solution was filtered and evaporated in a Buchi Rotavapor. A schematic drawing of the apparatus is shown in Figure 172.

3. Heterogeneous Flow Reactor Studies

The standard technique used in these studies of heterogeneous catalysts has been to gravity feed 1900 ml* of 9% formaldehyde solution through a vertical bed containing a weighed quantity of catalyst. (Figure 172) This catalyst bed is contained in a glass column completely surrounded by a heating tape plugged into a variable voltage transformer. Heating is controlled by use of a thermowatch induction coil (on the thermometer embedded in the catalyst) to operate an off-on relay which in turn controlls the power input to the variac. This system allows a control of $\pm$ 2°C in the temperature of the catalyst. A liquid level completely covering the catalyst is maintained by feeding the solution in at the same rate as it is withdrawn at the bottom.

- - - - -

* The total volume used in a run is 1900 ml, the volume to which a standard pint container of formaldehyde (37-40%) is diluted to yield 9% concentration.

To obtain an idea of the effect of space velocities (or contact time with the catalyst systems) on the products obtained requires good control of the flow rate. Use of a micrometer valve at the base of the column usually allows a good control over this flow of solution. Frequent adjustments to the valve are necessary when a new catalyst is being used because some leaching of catalyst by the hot water solution occurs in the early stages accompanied by a deposition of solids as the solution cools at the base of the column. This deposition may tend to clog the valve. If any co-catalyst is used, it is dissolved in the feed solution, preferably before adding the formaldehyde concentrate (37-40% formaldehyde in water with methanol stabilizer).

Before a run is begun the column is filled with water, the column is heated to the desired temperature and the solution allowed to flow through. At the end of a run, distilled water is used to displace the solution and the catalyst is allowed to cool in water, especially, if the catalyst is to be used for further flow reactions. In the more recent runs, carbon dioxide was bubbled into the effluent product.

The effluent is then vacuum evaporated in a Buchi Rotavapor under a water jet vacuum. Heating of the evaporator flask is done by a water bath heated to 55°C or lower. The solids obtained in this way are weighed and an aliquot of 50 grams is evaporated on a Steam Bath or in a vacuum oven at 80°C to remove paraformaldehyde. The residue from this evaporation gives a measure of the sugar formed and the loss in weight gives a measure of the paraformaldehyde present. A quicker method, which checks well with the two macro methods, involves heating about 100 mg on a weighed cover glass on a Fisher Johns Melting Point Apparatus until the odor of formaldehyde is gone or the melt ceases to bubble at 140-163°C. If a large amount of glyceraldehyde or glycolaldehyde is present, a considerable loss will occur, since a loss of glyceraldehyde of 50% was experienced with a pure sample heated to 140°C momentarily and then cooled. This loss seems to be minimized in the two macro methods by adding methanol (100-150 ml) to the solids before heating them. Apparently the methanol assists in depolymerization of the paraformaldehyde.

4. Heterogeneous Batch Hydrogenation Studies

Batch hydrogenation studies were carried out in a Parr, low pressure, Shaler type, catalytic apparatus available from Ace Scientific Co., Linden, N.J. The apparatus consists of an agitated glass reactor into which the catalyst, solvent and substrate are placed. Hydrogen is supplied from a reservoir containing a gauge. The speed of the reaction and extent of reaction are determined by observing in drop in pressure in the hydrogen reservoir.

5. Design of a Heterogeneous Flow Hydrogenation Unit

We have completed construction of a low pressure (1 atm) flow hydrogenation system for the heterogeneous hydrogenation of our formaldehyde condensation reaction products. The system is described in Figure 173. The aqueous sugar solution is fed from the reservoir into the reactor by nitrogen pressure. Hydrogen is metered into the reactor via a rotameter. The catalyst is supported by the distributor plate which consists of a porous glass disc which also serves to disperse the H_2 and sugar solution. The H_2 is separated from the glycerol solution in the gas-liquid separator. The glycerol solution is withdrawn through the liquid recovering flask. The H_2 exits through the gas receiving line and is metered through a wet test meter.

VIII. SUMMARY

A process for the production of glycerol has been identified and shown to be chemically feasible. The overall process consists of two chemical steps, first, selective self-condensation of formaldehyde to C_2 and C_3 sugars, and second, hydrogenation of the C_3 sugar product (glyceraldehyde and/or dihydroxyacetone) from stage I to glycerol. A separation step will be required in each step of the process, with recycle of the water solvent and other species such as unconverted feed materials.

Studies with the self-condensation of formaldehyde have shown that this reaction can be carried out both homogeneously or heterogeneously to yield a selective C_2-C_3 sugar product when the activity of the reaction system is carefully controlled. The reaction system exhibits an induction period which can be significantly shortened by employing, for example, a co-catalyst such as glucose. Homogeneous experiments indicate that the $Ca(OH)_2$/glucose system can be controlled to yield a selective product. Heterogeneous catalyst experiments using CaO/Al_2O_3 have shown that glyceraldehyde as well as glucose can be used as a "co-catalyst". This is significant since carrying on board glucose as a "co-catalyst" would result in a severe weight penalty for the process. It is planned to recycle part of the product for use as a "co-catalyst". High conversion levels and good selectivity have also been achieved with a Fe_2O_3/Al_2O_3 catalyst.

The feasibility of a low pressure hydrogenation step to convert C_3 sugars such as glyceroldehyde to glycerol has been demonstrated using a 5% Ru/carbon catalyst. Excellent hydrogenation rates were obtained at 80 to 100°C using hydrogen pressures ranging from 3 to 5 atmospheres. Kinetic studies indicate that the reaction is zero order in hydrogen pressure and first order in glyceraldehyde concentration. The fact that the rate of hydrogenation is independent of hydrogen pressure indicates that good rates should also be obtained at atmospheric pressure. Other studies indicated that the simultaneous use of two catalysts (Raney Nickel and PtO) produced an unusual synergistic effect, and that this combined catalyst system can also hydrogenate glyceraldehyde and C_2-C_3 sugars at mild conditions. However, the sugars solutions react with the nickel to product a soluble nickel complex which present a potential toxicity hazard not evident when using Ru/C.

Originally two approaches to glycerol synthesis were considered. Because of the success obtained in directing the formaldehyde condensation system to the production of lower sugars such as C_3 sugars, plus the lack of evidence to date that C_6 sugars can be selectively produced; we have concluded that the condensation of formaldehyde to C_3 sugars followed by a hydrogenation step is the most promising route to glycerol.

IX. FUTURE WORK

As a result of the accomplishments in the program, a number of problem areas have been elucidated which must be attacked before a practical glycerol synthesis process can be obtained. These areas are listed below.

- ● Catalyst Selectivity During CH_2O Self-Condensation

Both homogeneous and heterogeneous experiments indicate careful control of activity of system is critical to good selectivity, i.e., high production of C_2 and C_3 sugars. Thus further study of the complex CH_2O condensation reaction system is necessary to aid in achieving optimum selectivity.

- ● Activity Maintenance of Heterogeneous
  CH_2O Condensation Catalysts

The heterogeneous catalysts such as CaO/Al_2O_3 lose activity during the CH_2O condensation reaction. Data indicate that a major factor in this loss of activity is caused by loss of the calcium from the catalyst. This loss is surprising and presumedly results from the strong chelation properties of the sugars present in the reaction solution which remove the metal from the catalyst surface to form a homogeneous complex. Stable heterogeneous catalyst must be formulated or means to recover and recycle homogeneous catalysts developed.

- ● Reduction of C_3 Sugars to Glycerol

Although the Ru/C catalyst has demonstrated an ability to quantitatively hydrogenate glyceraldehyde to glycerol at mild conditions (80°C, 60 psig H_2), more work remains to be done in the hydrogenation area. An atmospheric pressure, flow process employing this catalyst must be developed. Catalyst activity maintenance must also be studied.

- ● Separation Processes

No extensive work has been done to date on separation processes for our two step process because up to recently the nature of the process to be employed was not defined. Now that our process is more clearly deliniated, detailed studies of separation techniques should be started. Our early decision to emphasize heterogeneous catalytic systems was based on the judgment that such systems would produce an effluent easier to separate than the product from a homogeneously catalyzed process. Consideration of separation processes should investigate possible means to separate and recover chelate complexes from the effluent of both process steps.

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APPENDIX 1

TABLE I

PRELIMINARY HOMOGENEOUS BATCH REACTOR STUDIES

Experiment Notebook Ref. 387-	Catalyst Main Catalyst	Co-Catalyst	Time	Temp.	Product wt % of CH_2O used	Moles CH_2O/Moles Cat/mole co-catalyst		Detailed G.C. Analysis of TMS Sugar Derivatives % C_3	pks	% $(C_3)_2$	pks	% C_4	pks	% C_5	pks	% C_6	pks	% above C_6	pks	See Fig.
IA	$CaCO_3$	--	Over Night	25°C	none		air	No GC Analysis												
IB	$CaCO_3$	--	Over Night	25°C	none		N_2	No GC Analysis												
IC	$Ca(OH)_2$	--	Over Night	25°C	18g. 100%	0.5/0.05/0	air	1.9	5	2.1	2	10.4	7	4.0	8	38.0	10	43.7	13	2
ID	$Ca(OH)_2$	--	Over Night	25°C	14g. 93%	0.5/0.05/0	N_2	No GC Analysis												
2-I	$Ca(OH)_2$	--	10 min.	80°C	23g. Syrup 100+%	0.5/0.05/0	air	1 peak at 35 mm (C_3 range)												
2-II	$Ca(OH)_2$	--	10 min.	75°C	14.9g. 100% Solid	0.5/0.05/0	N_2	3.4	1	--	--	22.4	4	10.3	2	50.0	3	13.8	1	3
3A	$CaCO_3$	--	Over Night	60°C	none		air	No GC Analysis												
3B (1)	$Ba(OH)_2$	--	Over Night	60°C	none		air	No GC Analysis												
3C	$Ca(OH)_2$	--	Over Night	60°C	5.9g. 39%	0.5/0.05/0	air	4.7	4	3.9	2	11.4	11	6.5	8	47.7	11	25.8	6	4
3D	$Ca(OH)_2$	--	Over Night	60°C	(2)		N_2	No GC Analysis												
14	$Ca(OH)_2$ 5g.	Glucose 30g.	Stepwise Addn. of CH_2O	60°C	58.5 100% Syrup	1.5/0.067/0.166	air	1.6	9	2.1	2	5.2	12	5.9	10	24.6	8	60.7	13	5
16	$Ca(OH)_2$ 10g.	Glucose 60g.	Stepwise Addn.	60°C	280.2g. 100% Syrup	6.0/0.134/0.332	air	5.3	8	4.2	2	9.4	14	9.0	11	32.0	8	40.0	8	6

(1) Product put through IRC-120 to remove Ca^{++}

(2) Product colorless until contacted with air, discarded

APPENDIX 2

TABLE II

FUNDAMENTAL INVESTIGATION OF THE
FORMALDEHYDE CONDENSATION IN A HOMOGENEOUS REACTION SYSTEM

No. of Exp.	CH_2O Present(1)	Catalyst $Ca(OH)_2$	Co-Catalyst 0.0013 m	Time, Minutes	Temp. °C	Weight	Product % Sugars in Solid(2)	% Yield as Sugars	Fig. No.
387-									
70-1	Yes	0.018 m	0.0018 Glucose	10	40				7
70-2	Yes	0.018 m	0.0036 Glucose	10	40				8
70-3	Yes	0.009 m	0.0036 Glucose	10	40				9
70-4	Yes	0.009 m	0.0018 Glucose	10	40				10
74-A	Yes	0.018 m	0.0018 Glucose	10	40				11
75-A	Yes	0.009 m	0.0018 Glucose	10	40				12
76-1	Yes	0.665g (0.009 m)	0.32g Glucose	10	60	5.0g	54	50	13
76-2	18%, 0.36 m	0.665g (0.009 m)	0.32g Glucose	10	60	12.6g	6.9	8.0	14
76-3	Yes	0.665g (0.009 m)	0.32g Glucose	1	60	6.2g	6.4	7.4	15
76-4	Yes	0.665g	0.32g Glucose	30	60	5.3g	84.2	82.6	16
76-5	37%	0.665g	0.32g Glucose	10	60	30.2g	2.7	3.8	17
76-6	Yes	0.665g	0.32g Glucose	5	60	4.2g	10.0	100	18
76-7	Yes	0.665g	0.162g Glyceraldehyde	10	60	6.2g	90.0	7.8	19
76-8	Yes	0.665g	0.32g Glucose	10	40	6.6g	2.7	3.3	20
76-9	Yes	0.333g (0.0045 m)	0.32g Glucose	10	40	6.2g	1.2	1.4	21
76-10	Yes	0.665g	0.32g Glucose	60	40	7.2g	11.7	15.7	22
76-11	Yes	0.333g	0.16g Glucose	10	40	6.7g	3.7	4.6	23
76-12	Yes	0.665g	0.16g Glucose	10	40	7 0g	3.2	4.2	24
76-13	Yes	0.333g	0.32g Glucose	10	40	6.4g	5.4	6.5	25
76-14	Yes	0.665g	None	10	60	6.7g	7.7	9.6	26
76-15	None	0.665g	0.32 Glucose	10	60	0.40g	91.8	100	27
76-16	None	0.665g	0.32 Mannose	10	60	0.30g	94.2	88.3	28
76-17	None	0.665g	0.32 Fructose	10	60	0.10g	91.2	28.5	29
76-18	None	0.665g	0.32 Galactose	10	60	0.30g	91.3	85.6	30
76-19	None	0.6b5g	0.27 Arabinose	10	60	0.20g	--	--	31
387-88(3)									
A	2.85 m	0.143 m	10g (0.057 m)	10	40	72.1g	20.5	17.3	32
B	2.85 m	10.6g	5g (0.029 m) Glucose	10	40	95.1g	7.5	8.3	33
C	2.85 m		5g (0.29 m)	1	40	93.7g	8.3	9.1	34

- - -
(1) Where present CH_2O concentration was normally 9%   0.18 m (5.4g) in the 60 ml of soln.
(2) Determined by micro-evap. technique on Fisher Johns apparatus.
(3) Large scale batches - used 2.85 m formaldehyde (as 37% soln.). These are similar to, but scaped up forms of, the regular fundamental batches.

TABLE III

HOMOGENEOUS FLOW REACTOR STUDIES

Experiment Notebook No. 387-	Catalyst — Main Catalyst	Co-Cat.	Contact Time	Temp	Product wt % (of CH₂O)	Conc. CH₂O	Volume of Feed	Apparatus	Detailed G.C. Analyses of TMS Sugar Derivatives % C₃	pks	% (C₃)₂	pks	% C₄	pks	% C₅	pks	% C₆	pks	% above C₆	pks	See Fig.
4	Ca(OH)₂ 13.4g 10m %	None	9 min	60°C		4.5%	1200 ml	5 meter Helix	No GC Analysis												
5	Ca(OH)₂ 21.2g 10m %	Glucose 5.0g 1m %	9 min	60°C	96.5g 100%	85.5g 4.5%	1900 ml	5 meter Helix	5.6	7	6.7	3	7.5	8	12.7	10	42.8	9	24.7	9	35
6	Ca(OH)₂ 21.2 10m %	Fructose 5g 1m%	15 min	60°C	78.5g 92%	85.5g 4.5%	1900 ml	5 meter Helix	8.0	2	6.2	2	11.6	8	15.0	5	42.4	10	16.6	6	36
7	Ca(OH)₂ 42.4g 10m %	Glyceralde-hyde 9g 1m %	8 min	60°C	57.5g 33.7%	171g 9.0%	1900 ml	5 meter H₂O ext. Helix MeOH ext.	-- (3 peaks in C₃ range only)	--	--	--	23.5	9	23.5	8	38.2	9	14.7	9	37
8	Ca(OH)₂ 42.4 10m %	Glucose 10g 1m %	8 min	60°C	198g Syrup 100%	171g 9.0%	1900 ml	10 meter Helix	No GC Analysis												
*9	Ca(OH)₂ 21.2 5m %	Glucose 10g 1m %	9 min	60°C	130.5g 76.5%	171g 9.0%	1900 ml	10 meter Helix	100	2	--	--	--	--	--	--	--	--	--	--	38
10	La(OH)₃ 72.2g 10m %	Glucose 10g 1m %	14 min	60°C	Considerable paraform	171g 9.0%	1900 ml	10 meter Helix	13.2	2	7.9	2	tr.		10.5	4	23.7	5	44.7	4	39
									ev. 4.8	8	2.8	4	5.9	13	6.3	13	21.9	6	58.3	15	40
*11	Ca(OH)₂ 21.2g 5m %	Glucose 10g 1m %	13 min	60°C	Syr. 111.5g 65% / Solid 24.7g 14.3%	171g 9.0%	1900 ml	10 meter Helix	Syrup 100	2	--	--	--	--	--	--	--	--	--	--	41
									Solid 3.5	3	2.7	3	--		--		--		--		42
*13(1)	Ca(OH)₂ 21.2g 5m %	Glucose 10g 1m %	13 min	60°C	Syr. 111.2g 66.5% / Solid 2.6g	171g 9.0%	1900 ml	10 meter Helix	Syrup 83	4	14.1	2	10.1	5	3.5	8	27.2	7	52.9	13	43
									Solid 100	2	tr.	2	tr.		2.8	3	--		--		44
20	Mg(OH)₂ 16.7g 5m %	Glucose 10g 1m %	10 min	60°C	A.(2) 6.3g 7.4%	85.5 171g 9.0%	1900 ml	10 meter Helix	A 2.1	7	tr.		tr.		tr.		tr.		tr.		45
					B. 6.0g 7.0%	85.5			B tr.		1.5	2	13.7	9	5.4	10	22.9	6	54.5	17	46
21	Mg(OH)₂ 33.4 10m %	Glucose 10g 1m %	10 min	60°C	19.8g 11.6% paraform 50.3g 29.4%	171g 9.0%	1900 ml	10 meter Helix	2.3	1	5.5	2	11.6	6	10.7	9	50.0	6	22.2	6	47
											8.4	2	3.4	6	27	7	41.7	7	17.2	7	
22	Th(OH)₄ 51.8g 2.5m %	Glucose 10g 1m %	10 min	60°C	13.7g 8% paraform 124g 73%	171g 9.0%	1900 ml	10 meter Helix	--	--	2.3	1	5.0	3	10.4	3	53.0	6	29.4	6	48
29	Mg(OH)₂ 16.7 5m %	Glucose 10g 1m %	10 min	80°C	30.2g 17.7% paraform 69.5g 41%	171g 9.0%	1900 ml	10 meter Helix	tr.		6.5	3	tr.		4.6	4	88.9	5	--	--	49

(1) Solution put through Rexyn ion exchange resin to remove Ca⁺⁺.
(2) A put through ion exchange resin to remove Ca⁺⁺, A and B were equal portions.

Tr = Trace

APPENDIX 4

TABLE IV

HETEROGENEOUS FLOW REACTION STUDIES YEILDS OF SUGARS AND PARAFORMALDEHYDE

Sample / reaction data

No	Notebook No.387-	Code*	Catalysts Composition	Co-catalyst	Space Velocity g.CH2O/hr.g.cat	Paraform %	Products Formed sugars grams	%	Total yield of CH2O grams	%
1	24	FC-0	Al_2O_3	Glucose 10g	0.18		29	17		
2	26	FC-0	Al_2O_3	None	0.18	26	4.0	2.3	47.8	28
3	19	FC-1	MgO/Al_2O_3	Glucose 10g	0.41	38.4	18.1	10.6	83.8	49
4	17	FC-2	CaO/Al_2O_3	None	0.41	12		12	41.6	24
5	18	FC-2	CaO/Al_2O_3	Glucose 10g	0.41	65	59.8	35	204.9	100
6	28	FC-2	CaO/Al_2O_3	Glucose 10g	0.08	46.5	91.5	53.5	195.9	100
7	31	FC-3	BaO/Al_2O_3	Glucose 10g	0.27	70.3	30.5	26.7	114	67
8	32	FC-3^u		Glyceraldehyde 5g	0.27	82.2	23.6	13.8	163.4	96
9	33	FC-3^u		Sorbitol 10g	0.27	74.6	15.0	8.8	142.6	83.4
10	35	FC-3^u		D-Xylose 8.6g	0.27	90.6	9.2	5.4	164	96
11	38	FC-3^u(90°C)		Glucose 10g	0.27	89.0	14.5	8.5	166.7	97.5
12	52	FC-4^u	La_2O_3/Al_2O_3	Glucose 10g	0.27	85.5	25	14.5	178	100
13	55	FC-4^u		Sorbitol 10g	0.27	90	11.9	7	165.4	97
14	57	FC-4^u		Mannitol 10g	0.27	87.6	16.6	9.7	166	97.3
15	59	FC-4^u		D-Xylose 8.6g	0.54	89.4	10.5	6.1	163.5	95.5
16	39	FC-5^u	Ce_2O_3/Al_2O_3	Glucose 10g	0.27	93	11.9	7	200	100
17	42	FC-5^u		None	0.27	94	tr.		160.2	94
18	46	FC-5^u		Sorbitol 10g	0.27	88.5	12.8	7.5	164	96
19	61	FC-6	CaO/SiO_2	Glucose 10g	0.27	57	63.3	37	19.6g 94 / 140.6g / 160.2	
20	62	FC-6^u		D-Xylose 8.6g	0.27	82.2	21	12.3	161.7	94.5
21	64	FC-6^u		L-Arabinose 8.6g	0.27	63.4	16.5	9.6	124.5	73
22	66	FC-6^u		Glucose 10g	0.27	40.8	24.2	14.2	110.9	65
23	67	FC-13	CaO/Al_2O_3	Glucose 10g	0.27	23	105	61.4	144.3	84.4
24	71	FC-13^u		Fructose 10g	0.27	57.4	73	42.6	213	100
25	72	FC-13^u		Glucose 10g	0.27	72	34.5	20.2	157	92

Gas Chromatographic Analysis of TMS Derivatives (by Figure number)

See Fig.	% C3	pks	% (C3)2	pks	% C4	pks	% C5	pks	% C6	pks	Sugars % above C6	pks
50	49.3	3	0.8	1	1.8	1	2.4	4	22.3	8	22.3	6
51	2.6	3	1.8	2	8.4	9	14.8	12	58.7	9	13.7	2
52	2.3	3	8.3	2	9.6	10	22.7	11	42.9	6	14.3	6
53	13.1 (1) 3 weak peaks 2) (evap)	5	12.2	3	11.9	8	19.2	8	19.2	9	24.4	6
54	14.1	5	5.1	2	7.1	3	6.1	3	14.1	7	53.5	12
55	Evap. 1.6	5	2.2	2	1.0	8	3.5	13	25.9	7	65.8	13
56	2.6	3	4.6	2	5.0	6	9.6	9	17.2	6	61.5	14
57	5.0	1	3.5	2	7.0	6	17.1	8	35.4	10	21.6	6
58	Evap.--	--	--	--	35.4	16	23.2	14	35.4	10	6.1	4
59	15.3	1	5.6	2	28.8	5	4.8	7	32.6	8	13.0	2
60	28.4	3	22.1	2	23.7	2	12.6	7	13.2	6	--	--
61	Evap. 5.8	3	8.7	3	1.7	2	11.0	7	65.4	8	7.3	6
62	9.3	5	6.9	3	1.7	6	3.5	5	74.0	8	4.6	2
63	79.2	2	8.4	1	0.9	1	1.8	2	--	--	15.8	4
64	10.1	3	8.4	4	2.8	1	1.7	1	46.4	8	30.7	5
65	32.6	4	6.8	3	2.7	5	0.8	3	51.6	7	5.4	3
66	Evap. 5.5	4	10.9	4	31.1	9	26.3	8	21.4	10	4.9	8
67	5.9	4	12.6	4	5.0	5	13.5	7	41.4	12	21.6	9
68	2.2	4	3.2	2	--	--	4.3	2	41.9	7	48.4	5
69	16.4	5	--	--	20.8	4	13.3	2	31.8	1	17.7	1
70	19.3	7	3.6	3	2.9	6	4.5	9	65.2	10	4.6	6
71	Evap. 3.4	4	3.4	4	2.7	4	7.7	7	22.4	9	60.5	15
72	1st 500 4.2	7	4.2	4	17.6	13	14.2	13	35.0	10	25.0	8
73	2nd eff 4.1	9	4.3	6	5.3	12	6.0	11	16.5	7	63.8	16
74	Evap. 0.9	6	14.2	2	4.6	14	7.3	10	25.6	12	47.3	16
75	2.7	3	25.6	3	2.4	5	25.0	5	43.7	8	30.5	10
76	3.5	4	8.7	3	2.2	3	80.0	11	5.4	6	--	--
77	5.1	6	1.1	3	1.4	9	2.5	6	9.0	9	80.9	15
78	Evap. 1.1	3	1.2	4	0.6	3	1.9	6	20.2	9	74.9	18
79	1.1	5	2.8	3	3.9	7	7.7	10	33.1	8	51.5	16
80	7.8	5	3.3	3	8.3	7	17.4	11	32.7	8	30.5	10
81	Evap. 1.3	7	10.8	3	5.2	12	10.6	14	38.4	8	33.7	12
82	9.6	3	0.0	3	1.5	3	10.5	9	54.2	11	15.1	9
83	27.6	7	7.7	3	5.1	2	6.2	4	22.1	7	31.3	10
84	Evap. 87.6	2	--	--	0.9	1	1.5	1	--	--	10.0	4

(2) footnote reference

APPENDIX 5

TABLE V

FUNDAMENTAL STUDIES OF THE FORMALDEHYDE CONDENSATION REACTION IN A HETEROGENEOUS SYSTEM

Exp. No.	Notebook No.	Code	Catalyst Composition	Co-Catalyst	Space Velocity gCH₂O/hr/g Cat	Products Formed Sugars gm.	%	Yield gm.	%	G.C. Analysis	Fig. No.
26	387-80-1(¹) 2	FC-13B	CaO/Al₂O₃, 20/30	Glucose 10g/5.7 mols. of CH₂O	0.27 0.27	3.9 5.6	12 15	32.5 37.6		Major portion C₂-C₃ region, much C₆ and above regions, some C₆ region / Large portion C₂-C₃ region, remainder scattered C₄,C₅-C₆ regions	85 86
	3				0.27	4.7	13	36.0		Some C₂-C₃ region, much C₆ and above regions (+ Glucose)	87*
	4				0.27	5.3	13	40.8		Some C₂-C₃ remainder scattered, much above C₆	88
	5				0.27	5.9	17	34.8		Evap. complex spectrum-very broad	89
	6				0.27	3.7	15	24.5		Some C₂-C₃ region much C₆ and above	90
	7&8				0.27	9.0	13	69.2		C₂-C₃ region exclusively	91
						TOTAL 275.4		(77)			
27	82	FC-13B^u( )	CaO/Al₂O₃, 20/80	Glycerald, 10g	0.27	44.7	26	141g	82	Evap. very broad spectrum	92
28	83	FC-13B^u	CaO/Al₂O₃, 20/80	Glycerald, 10g	0.54	32.1	18.8	184.5	100	Considerable C₂-C₃ region, traces C₄,C₅,C₆ and above	93
29	84	FC-13B^u	CaO/Al₂O₃, 20/80	Glucose, 10g	0.27	28.5	16.7	182.3	100	Considerable C₂-C₃ region, traces C₆ and above	94
30	85	FC-13B^u	CaO/Al₂O₃, 20/80	Fructose, 10g	0.27	19.6	11.5	174.7	100	No GC Analysis	95
31	86	FC-13B^u	CaO/Al₂O₃, 20/80	Glucose, 10g	0.17	21.6	12.6	187.2	100	C₂-C₃ only	96
32	87	FC-13B^u	CaO/Al₂O₃, 20/80	Mannose, 10g	0.27	43.4	25.3	202.9	100	C₂-C₃ only	97
33	91	FC-48	La₂O₃/Al₂O₃, 30/70	Glucose, 10g	0.27	11.5	6.8	188.5	100	C₂-C₃ only	98
34	92	FC-48^u	La₂O₃/Al₂O₃, 30/70	Glycerald, 10g	0.27	19.9	11.6	208.0	100	C₂-C₃ mainly some C₄ traces C₅ + C₆	99
35	93	FC-48^u	La₂O₃/Al₂O₃, 30/70	Glycerald, 10g	0.27	33.8	19.8	222.0	100	C₂-C₃ only	100
36	99	FC-10	Co-precip.	Glucose, 10g	0.27	21.1	12.5	145.5	85	C₂-C₃ only	101
37	101	FC-10^u	CaO/Al₂O₃, 20/80	Glycerald, 10g	0.27	32.6	19.1(⁴)	193.2	100	C₂-C₃ mainly, C₄,C₅,C₆ traces	102
38	103	FC-10^u	CaO/Al₂O₃, 20/80	387-13f,(³), 13g	0.27	12.5	7.3	181.0	100	C₂-C₃ only	103
39	98	FC-5B	Ce₂O₃/Al₂O₃, 30/70	Glucose, 10g	0.27	18	10.5	185.0	100	C₂-C₃ mainly-traces C₅	104
40	102	FC-5B	Ce₂O₃/Al₂O₃, 30/70	Glycerald, 30g	0.27	15.8	9.8(⁴)	133	100(⁵)	C₂-C₃ only	105
41	104	FC-5B	Ce₂O₃/Al₂O₃, 30/70		0.27		78		100	C₂-C₃ only	106
42	108	FC-14	CaSiO₃ pptd.	Glucose, 10g	0.27	13.8	8.1	146	85.5	C₂-C₃ only	107
43	106	FC-15	PbO/Al₂O₃ 20/80	Glucose, 10g	0.27	90.0	52.7	189	100	Considerable C₂-C₃, broad spectrum for remainder	108
44	107	FC-15^u	CaO/Al₂O₃ 20/80	Glycerald, 10g	0.27	55.2	32.3	202	100(⁵)	C₂-C₃ only	109
45	109	FC-18	PbO/Al₂O₃ 20/80	Glucose, 181g	0.43			191		Mainly C₆ region	110
46	111	FC-13B^u	CaO/Al₂O₃ 20/80	Glycerald, 10g	0.27	121	70.8	212	100	C₂-C₃ some C₄,C₅	111
47	113	FC-13B^u	CaO/Al₂O₃ 20/80	Glucose,()g	0.27	66	38.6	191	100	C₂-C₃ very large, trace C₄	112
48	115	FC-13B^u	CaO/Al₂O₃ 20/80	387-11f, ,12g	0.27	23.3	13.6	206	100	C₂-C₃ very large, trace C₄	113
49	415-1	FC-19^u	CoO/Al₂O₃ 20/80	Glyceral, 10g	0.27	19.7	11.5	186.3	100	C₂-C₃ only	114
50	2	FC-19^u	CoO/Al₂O₃ 20/80	Mannose, 10g	0.27	11.5	6.7	178	100	C₂ thru C₆ present	115
51	3	FC-19^u	CoO/Al₂O₃ 20/80	Glucose, 10g	0.27	15.9	7.4	173	100	C₂ thru C₆ present	116
52	4	FC-17	NiO/Al₂O₃ 20/80	Glyceral, 10g	0.27	16.6	9.3	175	100	Mainly C₂-C₃	117
53	5	FC-17	NiO/Al₂O₃ 20/80	Mannose, 10g	0.27	15.0	8.8	170	100	C₂ thru C₄	118
54	6	FC-17^u	NiO/Al₂O₃ 20/80	Glucose, 10g	0.27	13.3	7.8	155	90.5	C₂-C₃, trace C₄	119
55	7	FC-18	CuO/Al₂O₃ 20/80	Glyceral, 10g	0.27	10.2	5.9	188.2	100	C₂-C₃ only	120
56	8	FC-18^u	CuO/Al₂O₃ 20/80	Mannose, 10g	0.27	14.2	8.3	169.5	100		
57	9	FC-18^u	CuO/Al₂O₃ 20/80	Glucose, 10g	0.27	14.4	8.4	172	100	C₂-C₃, trace C₄	121
58	10	FC-20	ZnO/Al₂O₃ 20/80	Glyceral, 10g	0.27	31.4	18.4	224.5	100	C₂-C₃, some C₄	122
59	11	FC-20^u	ZnO/Al₂O₃ 20/80	Mannose, 10g	0.27	11.8	6.9	136	79.5	C₂-C₃ only	123
60	12	FC-20^u	ZnO/Al₂O₃ 20/80	Glucose, 10g	0.27	11.4	6.7	160.7	94.3	C₂ thru C₆ present	124
61	19	FC-16	Fe₂O₃/Al₂O₃ 20/80	Glyceral, 10g	0.27	85	49.7	180.3	100	C₂-C₃ present	125
62	19A	FC-16^u	Fe₂O₃/Al₂O₃ 20/80	Glyceral, 10g	0.27	167.2	97.8	205.7	100	Mainly C₂-C₄, some C₅	126
63	20	FC-16^u	Fe₂O₃/Al₂O₃ 20/80	Glyceral, 10g	0.27	76.5	44.7	207.6	100	C₂-C₄	127
64	14-1	FC-15B^u	PbO/Al₂O₃ 20/80	Glucose, 10g	0.27	68.2	39.9	150	87.8	Peaks in all Regions	128
65	14-2	FC-15B^u	PbO/Al₂O₃ 20/80	Glucose, 10g	0.27	53.3	31.2	167.2	97.8	Peaks in C₂-C₃, and C₆ Regions	129
66	14-3	FC-19^u	PbO/Al₂O₃ 20/80	Glucose, 10g	0.27	7.8	4.6	168	98.5	Peaks in C₂-C₃, and C₆ Regions	130
67	15-1	FC-15B^u	PbO/Al₂O₃ 20/80	Glycerald, 10g	0.27	84.5	49.5	205.5	100	No GC Analysis	
68	15-2	FC-15B^u	PbO/Al₂O₃ 20/80	Glycerald, 10g	0.27	58	33.9	174	100	No GC Analysis	
69	15-3	FC-15B^u	PbO/Al₂O₃ 20/80	Glycerald, 10g	0.27	60.7	35.5	182	100	No GC Analysis	
70	18-1	FC-15B^u( )	CaO/Al₂O₃ 20/80	Glycerald, 10g	0.27	30.6	17.9	160.5	94	Peaks in all regions	131
71	18-2	FC-13B^u	CaO/Al₂O₃ 20/80	Glycerald, 10g	0.27	41.3	24.2	211.5	100	Peaks in all regions	132
72	18-3	FC-13B^u	CaO/Al₂O₃ 20/80	Glycerald, 10g	0.27	25.4	14.8	170	100	Peaks in all regions	133
73	18-4	FC-13B^u	CaO/Al₂O₃ 20/80	Glycerald, 10g	0.27	18.6	10.9	200.8	100	Peaks in all regions	134
74	30	FC-24	Fe₂O₃/Al₂O₃	Glycerald, 10g	0.27	23.2	12.2	190.5	100	C₂-C₄	135
75	31	FC-26	Ca₃/Al₂O₃	Glycerald, 10g	0.27	21.4	13.5	158	92.4	C₂-C₄	136
76	33	CC-4	CaAl₂O₄ cement	Glycerald, 10g	0.27	21.4	70.8	57.5	33.6	Peaks in all regions, very complex	137

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(1) In Exp. 26 cuts were made every 500 ml to determine if any trend could be found during the flow experiments.

(2) u signifies used in previous experiment.

(3) 387-13f -homoflow product- GC analysis shows all C₂ + C₃ - recycle study.

(4) Sugar by micro method - S. Bath evap. gives substantially higher results - considerable C₂ + O₃ may be present.

(5) Homoflow product - recycle study.

(6) % of starting material.

(7) Preleached with conc. glucose solution.

APPENDIX 6

TABLE VI

INVESTIGATION OF ION EXCHANGE RESINS AS
CATALYSTS AND CATALYST SUPPORTS FOR THE CONDENSATION OF FORMALDEHYDE

Exp. No.	Notebook No. 387-	Code	Catalyst Comp.	Co-Catalyst	Space Velocity gCH₂O/hr/g Cat.	Products Formed				G.C. Analysis Interpretation	Fig. No.
						Total Yield of CH₂O		Sugars			
						Grams	%	Grams	%		
	37	RFC-1	Ca^{++} on IR120H	none	0.27	141	82.5	trace		C_2-C_6	138
	40	RFC-1^u		Glucose 10g	0.27	189.2	100	13.8	8.1	C_2-C_6	139
	44	RFC-2	Ca^{++} on IRC-50	none	0.108	134.6	79	trace		C_2-C_6	140
	47	RFC-2^u		none	0.216	182	100	--		No GC Analysis	141
	49	RFC-2^u		Glucose 1g	0.216	157.3	92	1.6	0.9	C_2-C_6	142
	51	RFC-2^u		Glucose 5g	0.216	195.2	100	7.4	4.3	C_2-C_6	143
	126	RFC-3	Amberlyst-15,50g/ cat.	--	0.27	131	76.5	0.0	0	C_2-C_3	
	129	RFC-3^u	Amberlyst-15,50g/ cat.	Glucose 10g	0.27	206.2	100	13.7	8.0	C_2-C_3	144
	135	RFC-3^u	Amberlyst-15,50g/ cat.	Glycerald 10g	0.27	203	100	12.4	7.2	C_2-C_3	145
	128	RFC-4	Amberlite IR 4B 100g	--	0.27	106.2	62.4	3.2	1.9	C_2-C_3	146
	130	RFC-4^u	Amberlite IR 4B 100g	Glucose 10g	0.27	224	100	11.0	6.5	C_2-C_3	147
	134	RFC-4^u	Amberlite IR 4B 100g	Glycerald 10g	0.27	207.2	100	30.0	17.6	C_2-C_3	148
	131	RFC-5	Ca^{++} on Amberlyst-15 (50g of resin)	--	0.27	129.7	76	0.0	--	C_2-C_4	149
	136	RFC-5^u	Ca^{++} on Amberlyst-15 (50g of resin)	Glucose 10g	0.27	172	100	12.8	7.5	C_2-C_3	150
	137	RFC-5^u	Ca^{++} on Amberlyst-15 (50g of resin)	Glyceral 10g	0.27	163.5	96	21.5	12.5	C_2-C_5,mainly C_4	151
	132	RFC-6	Pb on Amberlyst-15 (50g of resin)	--	0.27	154	90	15.4	9.0	C_2-C_3	152
	138	RFC-6^u	Pb on Amberlyst-15 (50g of resin)	Glucose 10g	0.27	188.2	100	36.2	21.0	C_2-C_3	153
	139	RFC-6^u	Pb on Amberlyst-15 (50g of resin)	Glyceral 10g	0.27	192	100	36.8	21.5	C_2-C_3	154
	140	RFC-8	Amberlite IRN-78 100g	--	0.27	205.8	100	0	--	C_2-C_3	155
	141	RFC-8^u	Amberlite IRN-78 100g	Glucose 10g	0.27	221.7	100	18.1	10.5	C_2-C_3	156
	142	RFC-8^u	Amberlite IRN-78 100g	Glyceral 10g	0.27	184.3	100	15.0	8.8	C_2-C_3	157
	143	RFC-9	OH^- Amberlite IRA-401S 100g	--	0.27	178	100	0	--	C_2-C_3	158
	144	RFC-9^u	OH^- Amberlite IRA-401S 100g	Glucose 10g	0.27	180	100	11.7	6.8	C_2-C_6,some C_6^+	159
	145	RFC-9^u	OH^- Amberlite IRA-401S 100g	Glyceral 10g	0.27	203.5	100	15.1	8.9	C_2-C_4	160
	415-23	RFC-11	Fe^{+3} on Amberlite IR-120	Glycerald 10g	0.27	167.0	97.7	21.0	12.6	C_2-C_3	161

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(u) Used in previous run.

APPENDIX 7

TABLE VII

INVESTIGATION OF MOLECULAR SIEVES AS CATALYSTS FOR THE CONDENSATION OF FORMALDEHYDE

Exp. No.	Notebook No.	Code	Catalyst	Co-Catalyst	Space Velocity gCH2O/hr/gm cat	Total Yield gms	%	Sugars gms	%	G.C. Analysis	Fig. No.
	415-26	Linde 5A	Ca^{++} exchanged Sieve	Glyceraldehyde 10 gm	0.27	118.9	69.5	23.6	19.8	Peaks in all regions	162
	415-26A	Linde 5A^U	Ca^{++} exchanged Sieve	Glyceraldehyde 10 gm	0.27	141	82.5	21.4	15.2	Peaks in all regions	163
	415-29	FC-23	Fe^{++} exchanged Sieve	Glyceraldehyde 10 gm	0.27	209.3	100	22.3	10.6	Peaks in all regions.	164

APPENDIX 8

TABLE VIII

Catalysts For Heterogeneous Flow Studies

Code	Composition		Al_2O_3	SiO_2	Preparation	Method[1]	Calcination[2] Temp°F	Hours
FC-0	Al_2O_3		8-10 mesh	--	--	--	--	--
FC-1	MgO/Al_2O_3	10/90	1/8" Pellets	--	$Mg(NO_3)_2 \cdot 6H_2O$	A	900	4
FC-2	CaO/Al_2O_3	20/80	1/8" Pellets	--	$Ca(NO_3)_2 \cdot 4H_2O$	A	900	4
FC-3	BaO/Al_2O_3	20/80	1/8" Pellets	--	$Ba(NO_3)_2$	A	900	4
FC-4	La_2O_3/Al_2O_3	30/70	1/8" Pellets	--	$La(NO_3)_3 \cdot 6H_2O$	A	900	4
FC-4B	La_2O_3/Al_2O_3	30/70	1/8" Pellets	--	$La(NO_3)_3 \cdot 6H_2O$	B	1500	6
FC-5	Ce_2O_3/Al_2O_3	30/70	1/8" Pellets	--	$Ce(NO_3)_3 \cdot 6H_2O$	A	900	4
FC-5B	Ce_2O_3/Al_2O_3	30/70	1/8" Pellets	--	$Ce(NO_3)_3 \cdot 6H_2O$	B	1500	6
FC-6	CaO/SiO_2	20/80	--	Davison 926-Sat Acid Washed	$Ca(NO_3)_2 \cdot 4H_2O$	B	900	4
FC-10	CaO/Al_2O_3	40/60	--	--	$Ca(NO_3)_2 \cdot 4H_2O$ $Al(NO_3)_3 \cdot 9H_2O$	C	900	4
FC-13	CaO/Al_2O_3	20/80	1/8" Pellets	--	$Ca(NO_3)_2 \cdot 4H_2O$	B	1500	5
FC-14	$CaSiO_3$	--	--	--	$CaCl_2$ Na_2SiO_3	D	900 1500	4 4
FC-15	PbO/Al_2O_3	20/80	1/8" Pellets	--	$Pb(Ac)_2 \cdot 3H_2O$	B	900	4
FC-16B	Fe_2O_3/Al_2O_3	20/80	1/8" Pellets	--	$Fe(NO_3)_3 \cdot 9H_2O$	B	900 1500	5 5
FC-17	NiO/Al_2O_3	20/80	1/8" Pellets	--	$Ni(NO_3)_3 \cdot 6H_2O$	B	900	4
FC-18	CuO/Al_2O_3	20/80	1/8" Pellets	--	$Cu(NO_3)_2 \cdot 3H_2O$	B	900	4
FC-19	CoO/Al_2O_3	20/80	1/8" Pellets	--	$Co(NO_3)_2 \cdot 6H_2O$	B	900	4
FC-20	ZnO/Al_2O_3	20/80	1/8" Pellets	--	$Zn(NO_3)_2 \cdot 6H_2O$	B	900	4
FC-23	Fe^{++} Sieve	--	--	--	$FeCl_2$	E	--	--
FC-24	Fe_2O_3/Al_2O_3	5/95	Powder	--	$Fe(NO_3)_3 \cdot 9H_2O$	F	1500	4
FC-26	CaO/Al_2O_3	5/95	Powder	--	$Ca(NO_3)_2 \cdot 4H_2O$	F	1600	12
CC-4	$CaAl_2O_4$	18/82	--	--	$CaAl_2O_4$ Cement	G	1600	17

[1] Preparation A Solution of salt in 100 ml H_2O allowed to stand over substrate for 1-3 hours. Poured off. Pellets dried at 230°F for SiO_2 or 280°F for Al_2O_3.

Preparation B Solution of salt in 100 ml H_2O allowed to stand 1 hour over substrate, then H_2O evaporated on Steam Bath. Pellets dried at 230°F for SiO_2 or 280°F for Al_2O_3.

Preparation C Coprecipitated $Ca(OH)_2$ and $Al(OH)_3$ from salts using NH_4HCO_3.

Preparation D $CaCl_2$ in solution of Na_2SiO_3 and the pptd. $CaSiO_3$ recovered.

Preparation E Sieves soaked twice in $FeCl_2$

Preparation F Solution of salt impregnated onto powder.

Preparation G Available from

[2] Calcined at lower temperature followed by higher temperature.

APPENDIX 9

TABLE IX

RESIN CATALYSTS FOR HETEROGENEOUS FLOW STUDIES

Code	Trade Name [1]	Type	Ion Exchanged	Preparation
RFC-1	Amberlite IR-120	Strongly Acidic	Ca^{++}	$CaCl_2$
RFC-2	Amberlite IRC-50	Weakly Acidic	Ca^{++}	$Ca(Ac)_2 \cdot H_2O$
RFC-3	Amberlyst-15	Strongly Acidic	None	--
RFC-4	Amberlite IR 4B	Weakly Basic	None	--
RFC-5	Amberlyst-15	Strongly Acidic	Ca^{++}	$Ca(Ac)_2 \cdot H_2O$
RFC-6	Amberlyst-15	Strongly Acidic	Pb^{++}	$Pb(Ac)_2 \cdot 3H_2O$
RFC-8	Amberlite IRN-78	Strongly Basic	None	--
RFC-9	Amberlite IRA-401S	Strongly Basic	OH^-	$NaOH$
RFC-11	Amberlite IR 120	Strongly Acidic	Fe^{+3}	$Fe(NO_3)_3 \cdot 9H_2O$

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[1] Rohm & Haas Co., Philadelphia, Pa.

APPENDIX 10

TABLE X

HYDROGENATION STUDIES USING NOBLE METAL CATALYSTS

Run No. 415	Catalyst, gms	Glyceraldehyde gms	Water, gm	Temp, °C	Total Time, Hrs.	Pressure, Psig Initial	Final	Induction Period
35	5% Pt/Al$_2$O$_3$ 1 gm	20	227	70-80	5	60	60	--
37-1	PtO$_2$ 0.06 gm	20	227	95-100	7	60	60	--
38	30-35% Ir/Al$_2$O$_3$ 0.2 gm	20	227	104	4.5	60	59.2	--
45	30-35% Ir/Al$_2$O$_3$ 0.5 gm	20	227	97	6	60	58.1	3 hrs
35-1	0.5% Rn/Al$_2$O$_3$ 1 gm	20	227	60	3	60	60	--
35-2	0.5% Rn/Al$_2$O$_3$ 1 gm	20	227	60	3	60	60	--
48	5% Rr/C 1 gm	20	227	115	6	60	55.2	2.5 hrs
41	5% Rn/C 2 gm	20	227	105	8	60	47.8	1 hr
42	5% Rn/C 5 gm	20	227	116	6.5	60	39.2	0.5 hr
43	5% Rn/C 2 gm	40	274	115	7	60	46	1 hr
44	5% Rn/C 2 gm	20	227	87	6	60	50.2	1.5 hrs
57	5% Rn/C 2 gm	20	227	104	6	30	21	1.5 hrs

APPENDIX 11

FIGURE 1

FIGURE 2

FIGURE 3

1-C

2-II

FIGURE 4

FIGURE 5

FIGURE 5

16

FIGURE 7

70-1

FIGURE 8

70-2

FIGURE 9

70-3

FIGURE 10

70-4

FIGURE 11

74-A

FIGURE 12

75-A

FIGURE 13

76-1

FIGURE 14

76-2

FIGURE 15

76-3

- 51 -

FIGURE 16

FIGURE 17

76-4

76-5

FIGURE 18

76-6

FIGURE 19

76-7

- 53 -

FIGURE 20

76-8

FIGURE 21

76-9

FIGURE 22

76-10

FIGURE 23

76-11

FIGURE 24

76-12

FIGURE 25

76-13

FIGURE 26

FIGURE 27

76-14

76-15

FIGURE 28

76-16

FIGURE 29

76-17

FIGURE 30

76-18

FIGURE 31

76-19

FIGURE 32

88-A

FIGURE 33

88-B

FIGURE 34

88-C

FIGURE 35

5

FIGURE 36

FIGURE 37

FIGURE 38

FIGURE 39

10 EVAP.

FIGURE 40

10-Vac. EVAP.

FIGURE 41

11-F

11-C-1-MECH.

FIGURE 42

13-S

FIGURE 43

FIGURE 44

13-C'-1

FIGURE 45

20-A

FIGURE 46

FIGURE 47

FIGURE 48

FIGURE 49

FIGURE 50

24-SYRUP

FIGURE 51

26-R. S.

FIGURE 52

FIGURE 53

FIGURE 54

18-DRIED

FIGURE 55

18-EVAP.

FIGURE 56.

FIGURE 57.

FIGURE 58

32-EVAP.

FIGURE 59

33-EVAP.

FIGURE 60

FIGURE 61

52-EVAP.

FIGURE 62

55-EVAP.

FIGURE 63

55

FIGURE 64

57

FIGURE 65

57-EVAP.

FIGURE 66

59-EVAP.

FIGURE 67

59

FIGURE 68

FIGURE 69

FIGURE 70

42-EVAP.

FIGURE 71

46

FIGURE 72

61-1st CUT

FIGURE 73

61

FIGURE 74

62-EVAP.

FIGURE 75

62

FIGURE 76

FIGURE 77

FIGURE 78

66-EVAP.

FIGURE 79

67-EVAP.

FIGURE 80

67

FIGURE 81

71-EVAP.

FIGURE 82

FIGURE 83

FIGURE 84

72-EVAP.

FIGURE 85

80-1

- 86 -

FIGURE 86

80-2

FIGURE 87

80-3

FIGURE 88

80-4

FIGURE 89

80-5-EV.

FIGURE 90

80-6

FIGURE 91

80-7

FIGURE 92

82-EV.

FIGURE 93

83

FIGURE 94

84-f₁

FIGURE 95

86-f₁

FIGURE 96

FIGURE 97

FIGURE 98

FIGURE 99

FIGURE 100

FIGURE 101

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101

FIGURE 102

103

FIGURE 103

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FIGURE 104

FIGURE 105

FIGURE 106

FIGURE 107

FIGURE 108

107

FIGURE 109

109

FIGURE 110

FIGURE 111

FIGURE 112

FIGURE 113

FIGURE 114

415-2

FIGURE 115

415-3

FIGURE 116

415-4

FIGURE 117

415-5

FIGURE 118

415-6

FIGURE 119

415-7

FIGURE 120

415-8

FIGURE 121

415-9

FIGURE 122

415-10

FIGURE 123

415-11

FIGURE 124

415-12

FIGURE 125

415-19

FIGURE 126

415-19-A

FIGURE 127

415-20

FIGURE 128

415-14-1

FIGURE 129

415-14-2

FIGURE 130

415-14-3

FIGURE 131

415-18-1

FIGURE 132

415-18-2

FIGURE 133

415-18-3

FIGURE 134

415-18-4

FIGURE 135

415-30

FIGURE 136

415-31

FIGURE 137

415-33

FIGURE 138

FIGURE 139

FIGURE 140

FIGURE 141

FIGURE 142

51-EVAP.

FIGURE 143

126

FIGURE 144

129

FIGURE 145

135

FIGURE 146

387-128

FIGURE 147

130

FIGURE 148

134

FIGURE 149

131

FIGURE 150

136

FIGURE 151

137

FIGURE 152

138

FIGURE 153

132

FIGURE 154

139

FIGURE 155

140

FIGURE 156

141

FIGURE 157

142

FIGURE 158

143

FIGURE 159

144

FIGURE 160

145

FIGURE 161

415-23
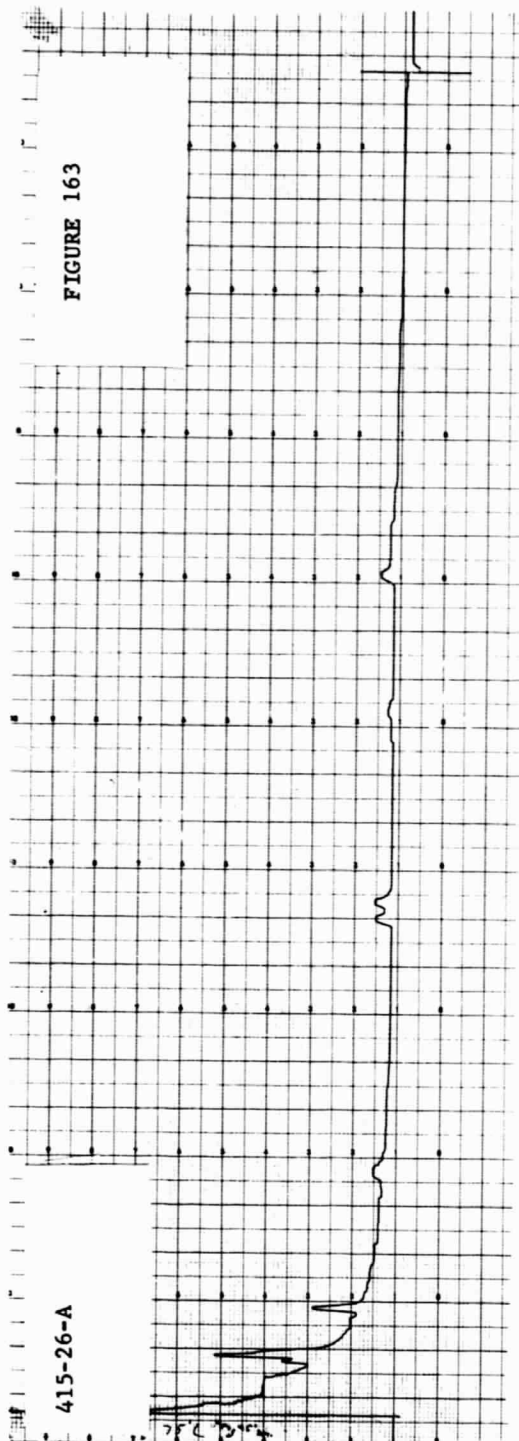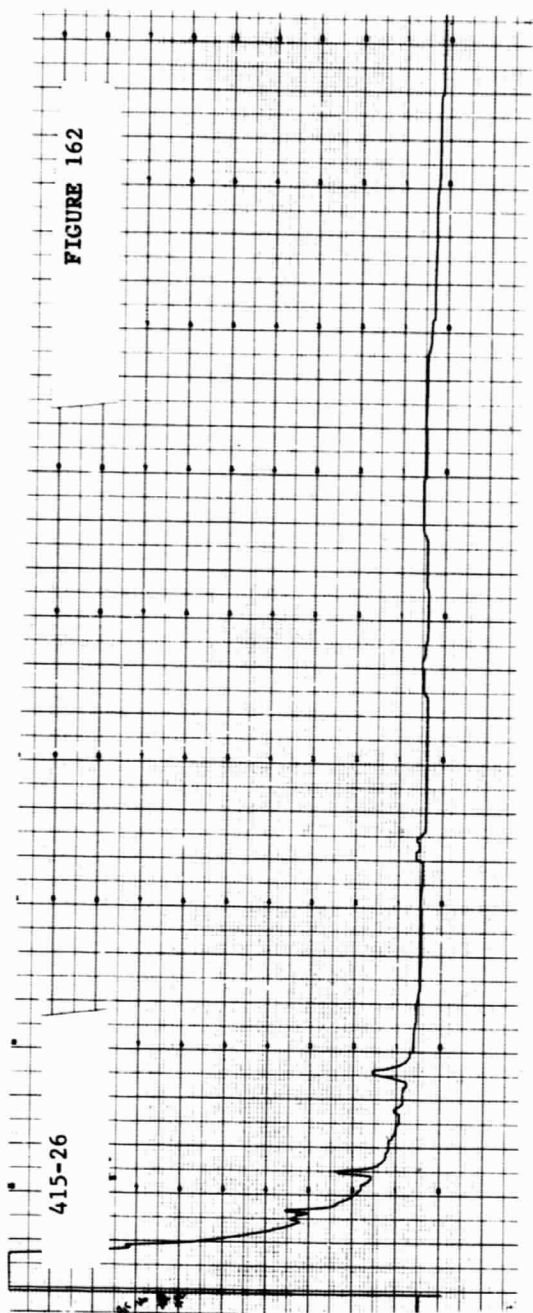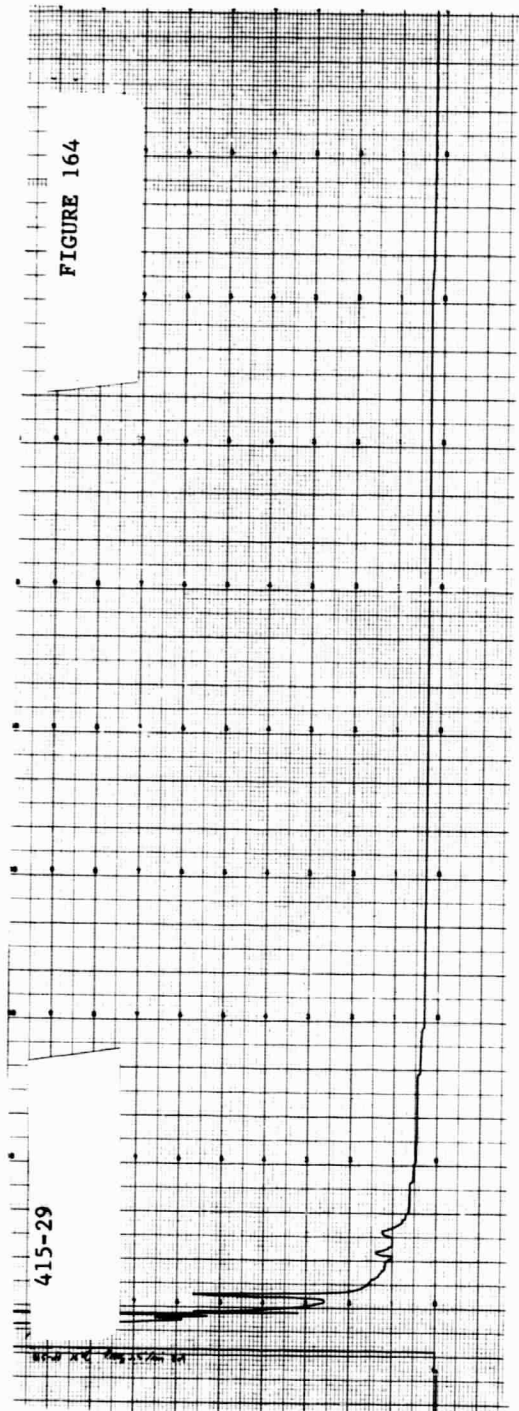
FIGURE 162

415-26

FIGURE 163

415-26-A

FIGURE 164

415-29

FIGURE 165

EFFECT OF CATALYST CONC. ON HYDROGENATION OF GLYCERALDEHYDE

▲ 415-42 - 5 gm
■ 415-41 - 2 gm
● 415-48 - 1 gm

Time, Hrs.

ΔP
(psig)

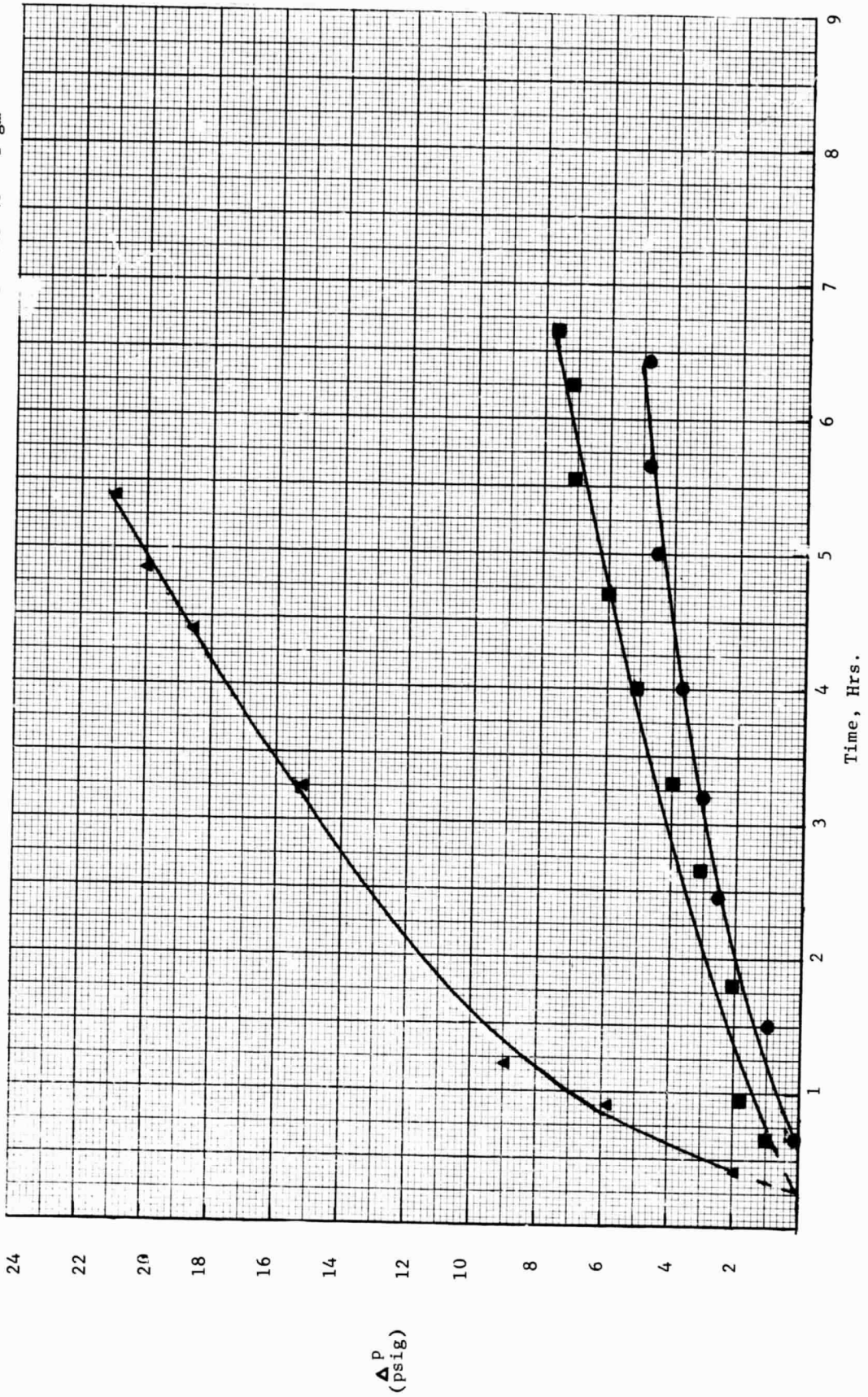FIGURE 166

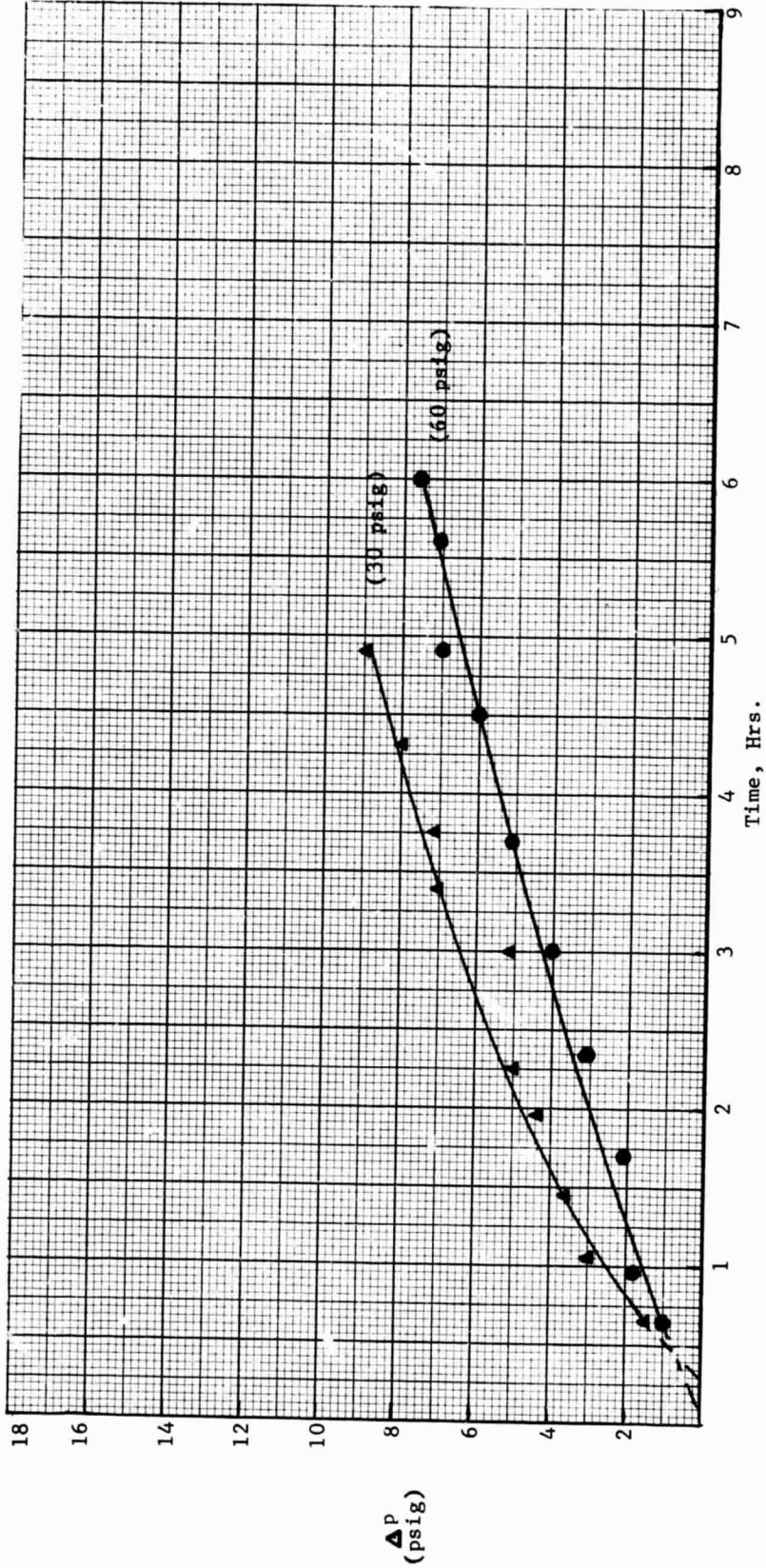EFFECT OF PRESSURE ON HYDROGENATION OF GLYCERALDEHYDE

FIGURE 167

EFFECT OF SUBSTRATE CONC. ON HYDROGENATION OF GLYCERALDEHYDE

▲ 415-41 - 20 gm

● 415-44 - 40 gm
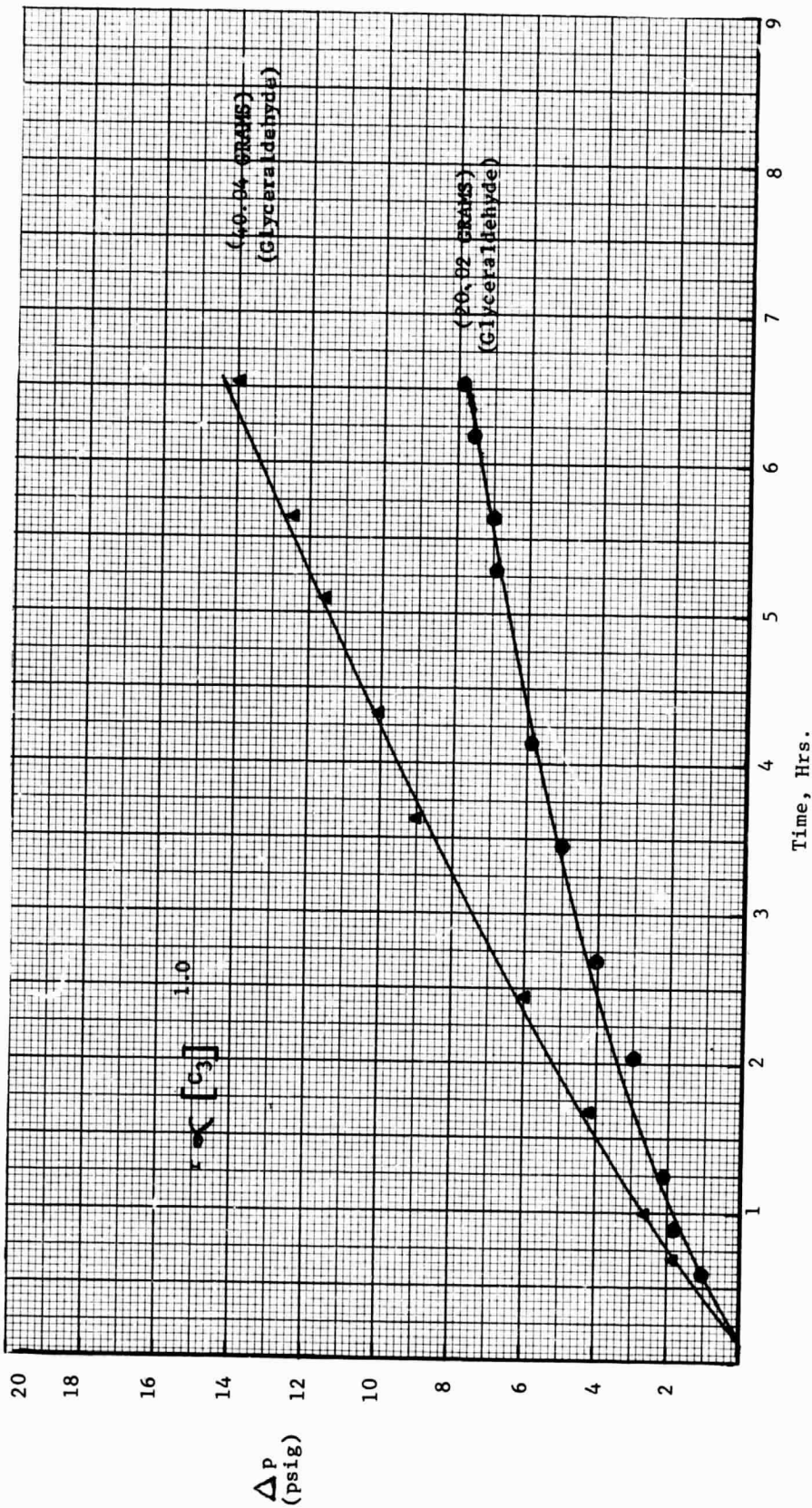
FIGURE 168

EFFECTS OF TEMPERATURE OF HYDROGENATION OF GLYCERALDEHYDE

FIGURE 172

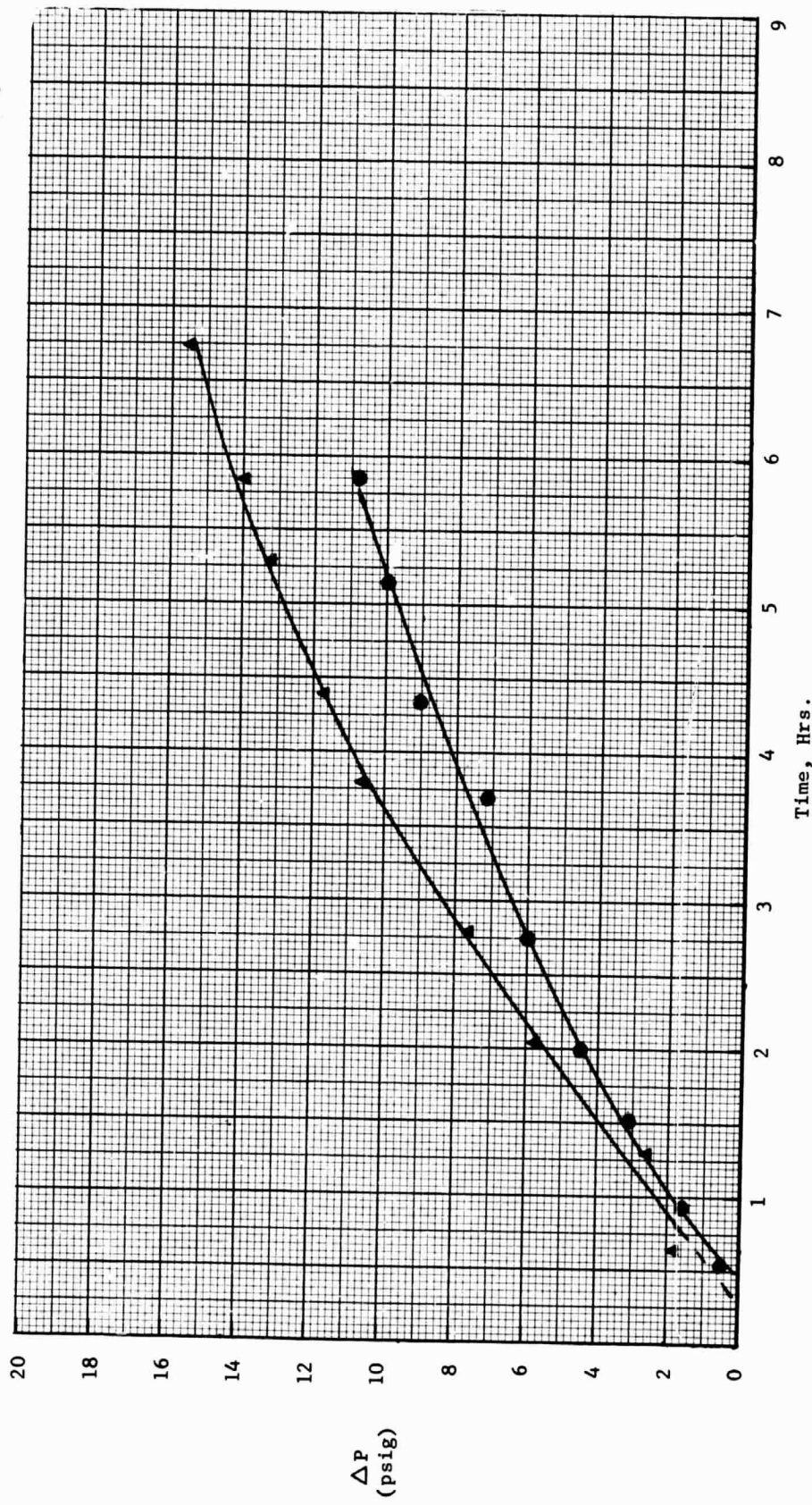### REACTION SYSTEMS

I. BATCH PROCESS

CATALYST
CH$_2$O
H$_2$O
CO-CATALYST

→ REACTOR →

RES. TIME - HOURS

→ FILTER →

CATALYST

→ EVAPORATOR →

H$_2$O

SUGARS
CO-CATALYST

II. HOMOGENEOUS FLOW REACTOR

CATALYST
CH$_2$O
H$_2$O
CO-CATALYST

→ PROPORTIONING PUMP →

10 METER SPIRAL

BATH
RESIDENCE TIME
6-15 MIN.

CO$_2$

→ FILTER →

CATALYST

→ EVAPORATOR →

H$_2$O

SUGARS
CO-CATALYST

III. HETEROGENEOUS FLOW REACTOR

CH$_2$O
H$_2$O
CO-CATALYST

→ CATALYST BED →

→ EVAPORATOR →

H$_2$O

SUGARS
CO-CATALYST
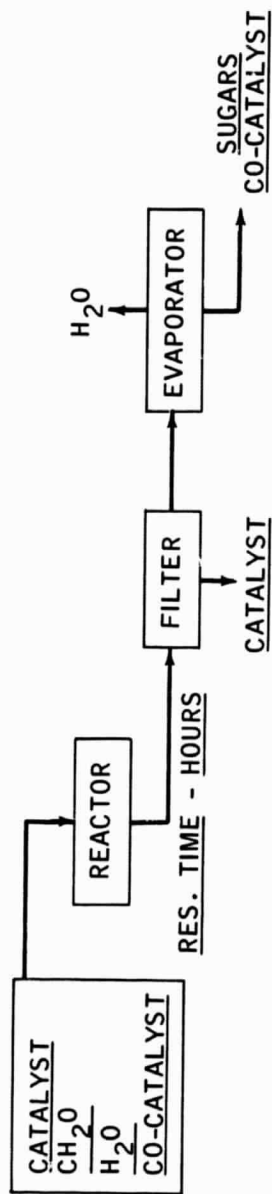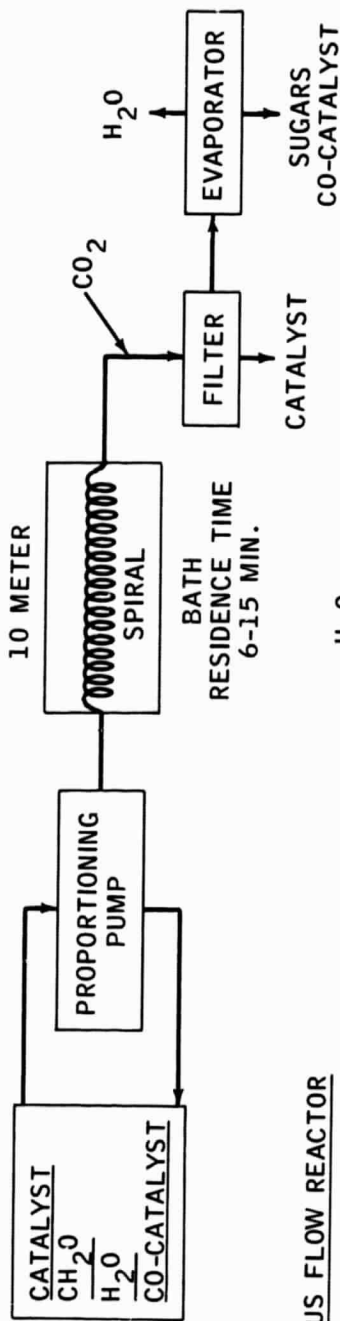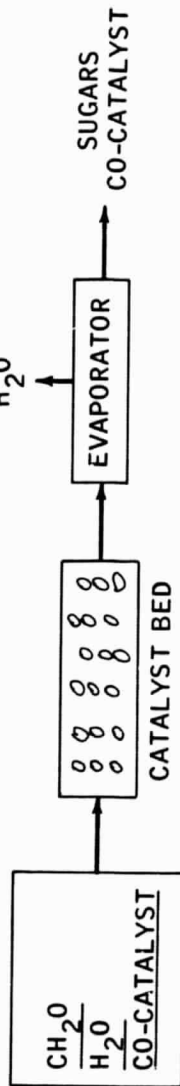
FIGURE 173

LOW PRESSURE FLOW HYDROGENATION SYSTEM
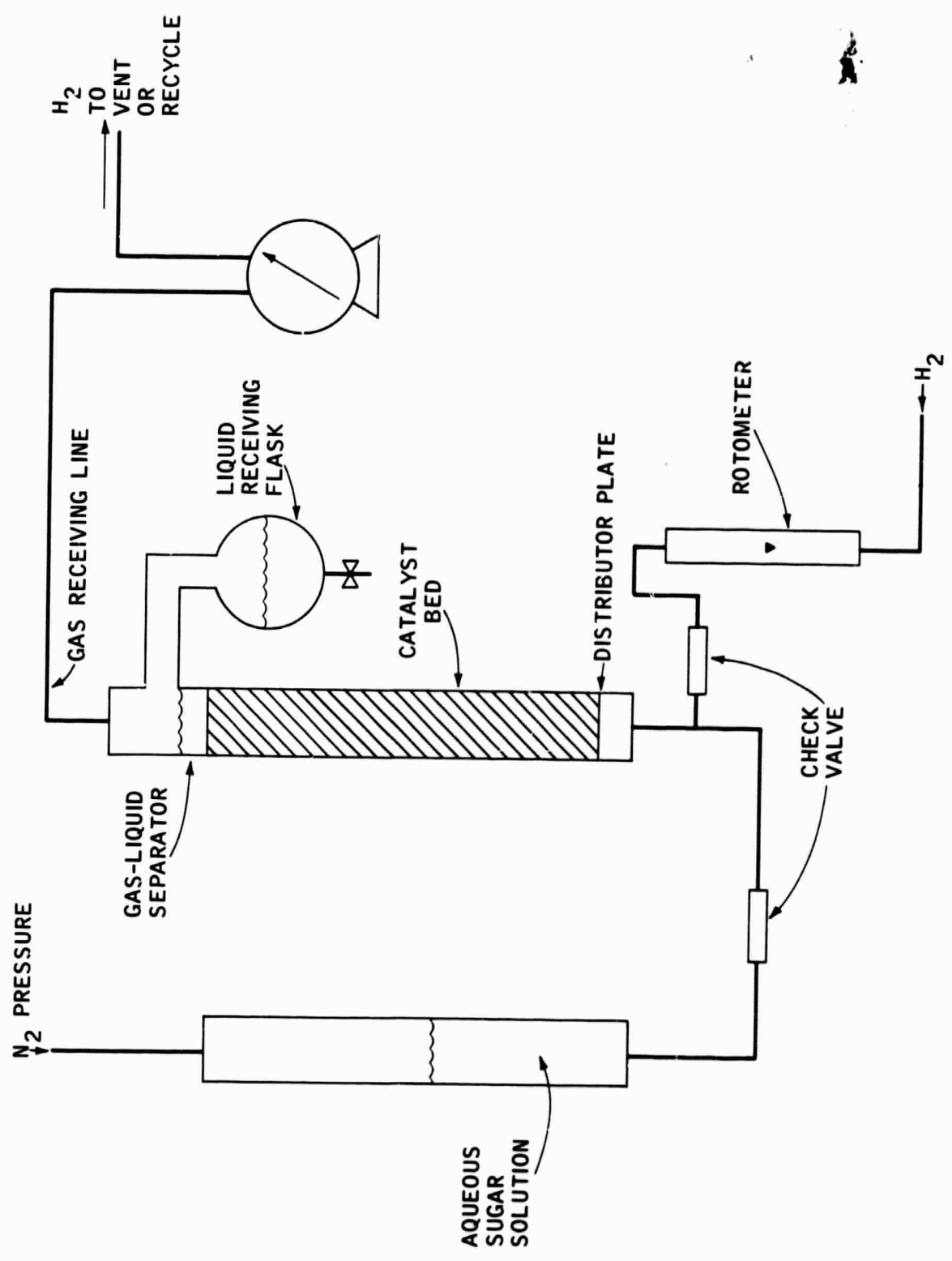
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13. ABSTRACT

A process for the production of glycerol has been identified and shown to be chemically feasible. The overall process consists of two chemical steps, first, selective self-condensation of formaldehyde to C_2 and C_3 sugars, and second, hydrogenation of the C_3 sugar product (glyceraldehyde and/or dihydroxyacetone) from stage I to glycerol. A separation step will be required in each step of the process, with recycle of the water solvent and other species such as unconverted feed materials.

Studies with the self-condensation of formaldehyde have shown that this reaction can be carried out both homogeneously or heterogeneously to yield a selective C_2-C_3 sugar product when the activity of the reaction system is carefully controlled. High conversion levels and good selectivity have been achieved with both a CaO/Al_2O_3 and a Fe_2O_3/Al_2O_3 catalyst. The feasibility of a low pressure hydrogenation step to convert C_3 sugars such as glyceraldehyde to glycerol has been demonstrated using a 5% Ru/carbon catalyst. Excellent hydrogenation rates were obtained at 80 to 100°C using hydrogen pressures ranging from 3 to 5 atmospheres.

Originally two approaches to glycerol synthesis were considered. Because of the success obtained in directing the formaldehyde condensation system to the production of lower sugars such as C_3 sugars, plus the lack of evidence to date that C_6 sugars can be selectively produced; we have concluded that the condensation of formaldehyde to C_3 sugars followed by a hydrogenation step is the most promising route to glycerol.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Glycerol						
Formaldehyde						
Closed loop life support systems						
Synthetic food						